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XX. *On a Theoretical and Experimental Investigation of the Stresses in a Radially Spoked Wire Wheel under Loads applied to the Rim.* By A. J. SUTTON PIPPARD, M.B.E., D.Sc., M.Inst.C.E., and W. E. FRANCIS, M.Sc., The University, Bristol*.

[Plate IV.]

IN a wheel of the artillery type the spokes consist of stout members rigidly attached both to the hub and to the rim. Under the action of loads applied to the rim these spokes are subjected to direct forces, either tensile or compressive, to transverse shearing forces and to bending moments: the resultant actions at any section of the rim consist of a bending moment, a radial shearing force, and a tangential tension or compression. An analysis of the stresses in such a wheel has already been given †.

In another type, known as the wire wheel, commonly used for motor cars and aeroplanes, the stout spokes of the artillery wheel are replaced by light wire members which are given initial tensions to enable them to resist compressive

* Communicated by the Authors.

† A. J. S. Pippard and J. F. Baker, "On the Stresses in a Spoked Wheel under Loads applied to the Rim," *Phil. Mag.* ii. pp. 1234-1253 (Dec. 1926).

forces. The number of spokes is large, ranging from thirty-two in a bicycle wheel to as many as one hundred and sixty-eight in a large aeroplane wheel.

The arrangement of the spokes varies in different makes of wheel: in some, as in a bicycle wheel, all spokes run tangentially to the hub. In others, including some of the largest, the spokes are all radial. Other types combine the two systems, some spokes being inclined and others radial. For the purpose of analysis, however, it may be assumed that all can be reduced to the case of a single system of radial spokes supporting the rim at a number of equidistant points.

Such a wheel is theoretically incapable of resisting loads on the rim except those acting radially, a slight rotation of the rim relative to the hub being required before tangential loads can be taken.

Therefore, in the theoretical and experimental analysis which follows, the case considered is that of a wheel with radial spokes under the action of a radial load on the rim. The practical application of the results obtained is left for discussion in a further paper. Since the spokes have practically no flexural rigidity, they are, in effect, pinjointed both to the hub and to the rim, and this is assumed in the analysis, which is divided into four parts as follows:—

Part I. Theoretical Analysis.

Part II. Arithmetical Solutions of Certain Cases.

Part III. Experimental Investigation.

Part IV. Discussion of Experimental Data and Summary.

PART I.

Theoretical Analysis.

A diagrammatic view of the problem to be considered is shown in fig. 1.

Let N be the number of spokes.

2θ , the angle between any two adjacent spokes.

R , the radius to the centroid of the rim.

R_0 , the hub radius.

I , the moment of inertia of the cross-section of the rim about its axis of bending.

a , the cross-sectional area of the rim.

a_0 , the cross-sectional area of a spoke.

E_1 , the modulus of elasticity of the rim.

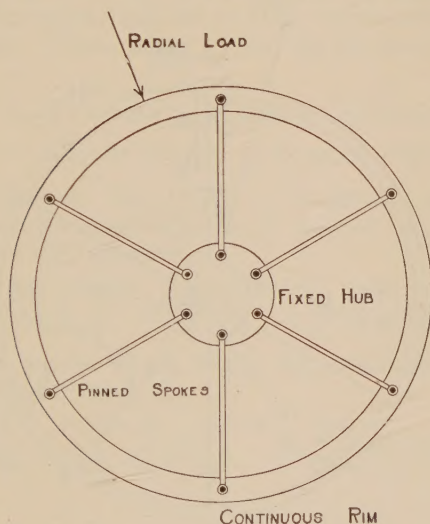
E_2 , the modulus of elasticity of the spokes.

The wheel is a framework having a number of redundant members and resultant actions.

In order to connect the hub to the rim two spokes only are necessary, the remaining $(N-2)$ being redundant. In addition, the continuity of the rim introduces three redundant resultant actions, since the rim could be cut at any section without destroying the effectiveness of the frame.

The essential or statically determinate frame, therefore, consists of a rim severed at one section, connected to the hub by two spokes; the redundant forces and moments to be determined are the axial loads in $(N-2)$ spokes, a bending

Fig. 1.



moment in the rim, a tangential, and a radial force in the rim.

Let the tensile loads in the spokes be $T_1, T_2 \dots T_N$, as shown in fig. 2, and let the radial load P act inwards between the N th and $(N-1)$ th spokes, so that it makes an angle ϕ with the former. These two spokes will be taken as the essential members of the frame.

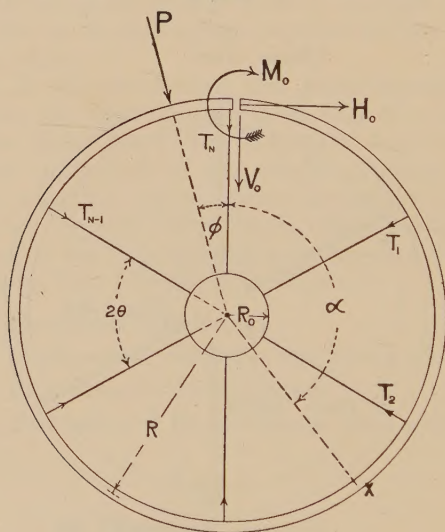
Imagine the rim to be cut through immediately to the right of the N th spoke, and let the resultant actions in the rim at this section be replaced by the bending moment M_0 , the tangential force H_0 , and the radial shear V_0 . Then,

if U be the total strain-energy in the wheel due to P , we can write

$$\left. \begin{aligned} \frac{\partial U}{\partial V_0} &= 0, \\ \frac{\partial U}{\partial H_0} &= 0, \\ \frac{\partial U}{\partial M_0} &= 0, \\ \frac{\partial U}{\partial T_1} = \frac{\partial U}{\partial T_2} = \dots = \frac{\partial U}{\partial T_{N-3}} = \frac{\partial U}{\partial T_{N-2}} &= 0. \end{aligned} \right\} \quad (1)$$

These conditions, together with those for the static equilibrium of the wheel, provide sufficient equations for a

Fig. 2.



complete solution of the problem. Any stresses in the wheel due to the initial tensioning of spokes are additional to those produced by the external load, and the final stress at any point in the wheel is the algebraic sum of the stresses induced by the two separate systems.

The conditions for the static equilibrium of the rim are:—

$$T_1 \sin 2\theta + T_2 \sin 4\theta + \dots + T_{N-1} \sin 2(N-1)\theta = P \sin \phi, \quad (2)$$

$$T_1 \cos 2\theta + T_2 \cos 4\theta + \dots + T_{N-1} \cos 2(N-1)\theta + T_N = -P \cos \phi. \quad (3)$$

The equation of moments is automatically satisfied, since the spokes and the line of action of P are all radial.

In calculating the strain-energy of the wheel, the following assumptions are made :—

- (1) The hub is rigid.
- (2) The terms due to the curvature of the rim can be neglected, since the curvature is small compared with the cross-sectional dimensions of the rim.
- (3) The contribution from direct compression of the rim is negligible.
- (4) The energy due to transverse shear in the rim is negligible.

Let X in fig. 2 be any point on the rim between the p th and $(p+1)$ th spokes, and let x be at a radial distance α from the N th arm. Then, when $\alpha < 2\pi - \phi$, the bending moment at X is

$$M_x = M_0 + H_0 R(1 - \cos \alpha) - V_0 R \sin \alpha - R\{T_1 \sin(\alpha - 2\theta) + T_2 \sin(\alpha - 4\theta) \dots T_p \sin(\alpha - 2p\theta)\}. \quad (4)$$

When $\alpha > 2\pi - \phi$, the term $-PR \sin(\alpha + \phi)$ must be added. Then, for the segment of the rim between $\alpha = 2p\theta$ and $\alpha = 2(p+1)\theta$, we have

$$\left[\frac{\partial U}{\partial M_0} \right]_{2p\theta}^{2(p+1)\theta} = \frac{R}{E_1 I} \int_{2p\theta}^{2(p+1)\theta} M_x \frac{\partial M_x}{\partial M_0} d\alpha,$$

and for the whole wheel, since the strain-energy of the spokes does not involve M_0 ,

$$\frac{\partial U}{\partial M_0} = \sum_{p=0}^{p=N-1} \frac{R}{E_1 I} \int_{2p\theta}^{2(p+1)\theta} M_x \frac{\partial M_x}{\partial M_0} d\alpha = 0.$$

Similarly,

$$\frac{\partial U}{\partial H_0} = \sum_{p=0}^{p=N-1} \frac{R}{E_1 I} \int_{2p\theta}^{2(p+1)\theta} M_x \frac{\partial M_x}{\partial H_0} d\alpha = 0,$$

and

$$\frac{\partial U}{\partial V_0} = \sum_{p=0}^{p=N-1} \frac{R}{E_1 I} \int_{2p\theta}^{2(p+1)\theta} M_x \frac{\partial M_x}{\partial V_0} d\alpha = 0;$$

upon integration and summation these lead to the following equations :—

$$2\pi(M_0 + RH_0) - R(T_1 + T_2 + \dots T_N) = PR, \quad \dots \quad (5)$$

$$\pi H_0 + \theta\{T_1 \sin 2\theta + 2T_2 \sin 4\theta + 3T_3 \sin 6\theta + \dots$$

$$+ (N-1)T_{N-1} \sin 2(N-1)\theta\} = \frac{P}{2} (2\pi - \phi) \sin \phi, \quad \dots \quad (6)$$

$$\pi V_0 - \theta \{ T_1 \cos 2\theta + 2T_2 \cos 4\theta + 3T_3 \cos 6\theta + \dots NT_N \} \\ = \frac{P}{2} (2\pi - \phi) \cos \phi. \quad (7)$$

Now consider the formation of the second group of strain-energy equations of the type $\partial U / \partial T_r = 0$.

The loads in the r th, $(N-1)$ th, and N th spokes are functions of T_r , and so

$$\frac{\partial U}{\partial T_r} = \frac{1}{a_0 E_2} \int_0^L \left(T_r + T_{N-1} \frac{\partial T_{N-1}}{\partial T_r} + T_N \frac{\partial T_N}{\partial T_r} \right) dx \\ + \sum_p \left[\frac{R}{E_1 I} \int_{2p\theta}^{2(p+1)\theta} M_x \frac{\partial M_x}{\partial T_r} d\alpha \right] = 0,$$

where L is the length of the spoke from hub to rim.

The summation in the second integral extends over the following limits:—

Terms in M_0 , H_0 , and V_0 from $p=r$ to $p=(N-1)$.

Terms in T_q where $q \leq r$, from $p=r$ to $p=(N-1)$,

and where $q > r$, from $p=q$ to $p=(N-1)$.

It should be noted that $\partial M_x / \partial T_r$ is constant from $\alpha = 2r\theta$ to $\alpha = 2(N-1)\theta$, but includes an additional term between $\alpha = 2(N-1)\theta$ and $\alpha = 2N\theta$, since T_{N-1} is a function of T_r .

Upon integration and reduction this leads to

$$T_r = -G \left[H_0 \{ 2(r+1)\theta \sin 2r\theta \} \right. \\ + V_0 \{ 2\theta \sin 2r\theta \cot 2\theta - 2r\theta \cos 2r\theta \} \\ - \frac{2(m_0 + H_0)}{\sin 2\theta} \{ \sin 2\theta + \sin 2r\theta - \sin 2(r+1)\theta \} \\ - T_N \sin 2r\theta \{ 2\theta \cot 2\theta - 1 \} \\ + T_1 \{ \sin 2(r-1)\theta - 2(r-1)\theta \cos 2(r-1)\theta \} \\ + T_2 \{ \sin 2(r-2)\theta - 2(r-2)\theta \cos 2(r-2)\theta \} \\ + \dots + T_{r-1} \{ \sin 2\theta - 2\theta \cos 2\theta \} \\ + \frac{P \sin 2r\theta}{\sin 2\theta} \{ \sin (2\theta - \phi) - (2\theta - \phi) \cos (2\theta - \phi) \} \left. \right] \\ - T_{N-1} \frac{\sin 2r\theta}{\sin 2\theta} + T_N \frac{\sin 2(r+1)\theta}{\sin 2\theta}, \quad (8)$$

where m_0 is written for M_0/R , and

$$G = \left(\frac{R^3}{E_1 I} \times \frac{a_0 E_2}{2L} \right). \quad \dots \quad (9)$$

In equation (8) r has successively all values from 1 to $(N-2)$. It will be seen from the foregoing equations that the elastic properties of the wheel are defined by the term G , which forms a convenient basis for the discussion of theoretical and experimental results.

Equations (2), (3), (5), (6), (7), and the $(N-2)$ equations given by (8), provide a complete theoretical solution of the problem, since, by putting $r=1$ in (8), a value of T_1 is found in terms of H_0 , V_0 , (m_0+H_0) , T_{N-1} , and T_N . By putting $r=2$, T_2 is then found in terms of the same quantities. Thus, by successive substitution in (8), all the values $T_1 \dots T_{N-2}$ can be determined as functions of the same five quantities.

Equations (2), (3), (5), (6), and (7) are then sufficient for the evaluation of these, and they can be resubstituted to give absolute values of T_1 etc.

The work, however, is laborious, very great accuracy being essential, since the final equations yield large numbers which differ by small amounts. Many attempts have been made to recast the equations in a more practicable form, but with only limited success.

An explicit solution for (m_0+H_0) was, however, obtained as follows :—

By summing all the equations of type (8) from $r=1$ to $r=(N-2)$, an expression for $(T_1+T_2+\dots T_N)$ was obtained which was dependent only on (m_0+H_0) and P , and by substituting this in (5) a general value of (m_0+H_0) was found to be

$$\frac{(m_0+H_0)}{P} = \frac{2(1-\cos 2\theta) + G(2\theta + \sin 2\theta) - G\{\sin(2\theta - \phi) + \sin \phi + \phi \cos(2\theta - \phi) + (2\theta - \phi) \cos \phi\}}{2\pi\{2(1-\cos 2\theta) + G(2\theta + \sin 2\theta)\} - 4NG(1-\cos 2\theta)} \quad (10)$$

From this (m_0+H_0) can be directly evaluated, and the final solution involves four instead of five simultaneous equations.

Unfortunately the same method does not lead to explicit solutions for the other quantities involved, and when $T_r \sin 2r\theta$, $T_r \cos 2r\theta$, $rT_r \sin 2r\theta$, and $rT_r \cos 2r\theta$ are summed, residual series in $T_1 \dots T_{N-2}$ appear which cannot be evaluated.

The case of a rigid rim.—For the case of a rigid rim $G=0$, and a solution is readily obtained.

From equation (8)

$$T_r = -T_{N-1} \frac{\sin 2r\theta}{\sin 2\theta} + T_N \frac{\sin 2(r+1)\theta}{\sin 2\theta},$$

and substitution in the static equations leads to

$$T_r = -\frac{2P}{N} \cos (2r\theta + \phi) \quad . \quad . \quad . \quad (11)$$

for all spokes from $r=1$ to $r=N$.

Equations (5), (6), and (7) then give

$$(m_0 + H_0) = \frac{P}{2\pi}, \quad . \quad . \quad . \quad (12)$$

$$H_0 = \frac{P}{2\pi} \{(\pi - \phi - \theta) \sin \phi - \theta \cos (2\theta + \phi) \operatorname{cosec} 2\theta\}, \quad (13)$$

$$V_0 = \frac{P}{2\pi} \{(\pi - \phi - \theta) \cos \phi - \theta \sin (2\theta + \phi) \operatorname{cosec} 2\theta\}. \quad (14)$$

The case of a non-rigid rim.—When the rim is not rigid the general equations are in most instances too complicated for manipulation; but there are two symmetrical cases, viz., $\phi=0$ and $\phi=\theta$, which lead to somewhat simpler results, and provide all the essential information.

The first case, $\phi=0$, gives the maximum compressive load which can occur in a spoke, and $\phi=\theta$ gives the maximum bending moment which can occur in the rim.

The general case when $\phi=0$.—From considerations of symmetry $T_1=T_{N-1}$, $T_2=T_{N-2}$, etc., and equation (3) then gives

$$T_1 \cos 2\theta + T_2 \cos 4\theta + \dots = -\frac{1}{2}(P + T_N),$$

where the left-hand side of the equation includes the spokes in one half of the wheel except T_N . Also, equation (7) gives

$$V_0 - (T_1 \cos 2\theta + T_2 \cos 4\theta + \dots) = P + T_N,$$

where the term in brackets is the same as in the equation above. Hence

$$V_0 = \frac{1}{2}(P + T_N), \quad . \quad . \quad . \quad (15)$$

a result which is also obvious from a consideration of the conditions of equilibrium at the cut section of the rim.

Using the value of T_N from equation (15), and putting $T_{N-1}=T_1$, we obtain from equation (8)

$$\begin{aligned}
 T_r = & -G[H_0(2r\theta \sin 2r\theta) - V_0(2r\theta \cos 2r\theta) \\
 & + V_0 \sin 2r\theta - 2(1 - \cos 2r\theta)(m_0 + H_0) \\
 & + T_1 \{ \sin 2(r-1)\theta - 2(r-1)\theta \cos 2(r-1)\theta \} \\
 & + T_2 \{ \sin 2(r-2)\theta - 2(r-2)\theta \cos 2(r-2)\theta \} \\
 & + \dots + T_{r-1} \{ \sin 2\theta - 2\theta \cos 2\theta \}] + (2V_0 - P) \cos 2r\theta;
 \end{aligned}$$

. . . (16)

also, from (10),

$$\begin{aligned}
 & (m_0 + H_0) \\
 & = P \left[\frac{1 - \cos 2\theta}{\pi \{ 2(1 - \cos 2\theta) + G(2\theta + \sin 2\theta) \} - 2NG(1 - \cos 2\theta)} \right].
 \end{aligned}$$

. . . (17)

From equation (16)

$$\begin{aligned}
 T_1 = & -G[H_0 \cdot 2\theta \sin 2\theta - V_0(2\theta \cos 2\theta - \sin 2\theta) \\
 & - 2(1 - \cos 2\theta)(m_0 + H_0)] + T_N \cos 2\theta,
 \end{aligned}$$

and so

$$H_0 = \frac{T_N \cos 2\theta - T_1}{G \cdot 2\theta \sin 2\theta} + V_0 \left(\cot 2\theta - \frac{1}{2\theta} \right) + \frac{1 - \cos 2\theta}{\theta \sin 2\theta} (m_0 + H_0).$$

. . . (18)

The equations (15), (17), and (18) express the rim reactions in terms of T_1 and T_N , so that all the spoke loads can be found as functions of these terms. The equations of static equilibrium then provide the absolute solution.

The rigid rim when $\phi=0$.—When $\phi=0$ the solution for the rigid rim is

$$\left. \begin{aligned}
 T_r &= -\frac{2P}{N} \cos 2r\theta, \\
 (m_0 + H_0) &= \frac{P}{2\pi}, \\
 H_0 &= -\frac{P}{2N} \cot 2\theta, \\
 V_0 &= P \left(\frac{N-2}{2N} \right).
 \end{aligned} \right\} \dots \dots (19)$$

The general case when $\phi=\theta$.—To obtain the solution for this case it is advisable to express the equations in terms of

the rim reactions immediately to the right of the load, instead of just to the right of the N th spoke as hitherto.

Let M_0' be the bending moment in the rim to the right of the load, H_0' the tangential force, and V_0' the radial shearing force at the same point.

Then we can write :

$$V_0' = V_0 \cos \theta + H_0 \sin \theta - T_N \cos \theta,$$

$$H_0' = H_0 \cos \theta - V_0 \sin \theta + T_N \sin \theta,$$

$$M_0' = M_0 + H_0 R(1 - \cos \theta) + V_0 R \sin \theta - RT_N \sin \theta,$$

and from these we obtain

$$(m_0 + H_0) = (m_0' + H_0'),$$

$$V_0 = T_N + V_0' \cos \theta - H_0' \sin \theta,$$

$$H_0 = H_0' \cos \theta + V_0' \sin \theta.$$

Substituting these values in equations (5), (6), and (7), we find

$$2\pi(M_0' + RH_0') - R(T_1 + T_2 + \dots T_N) = PR,$$

$$H_0' = -\frac{1}{N} [T_1 \sin 3\theta + 2T_2 \sin 5\theta \\ + \dots (N-1)T_{N-1} \sin (2N-1)\theta],$$

$$V_0' = \frac{1}{N} [T_1 \cos 3\theta + 2T_2 \cos 5\theta \\ + \dots (N-1)T_{N-1} \cos (2N-1)\theta] + \frac{P}{2\pi} (2\pi - \theta),$$

while the static equations can be rewritten

$$T_N \sin \theta + T_1 \sin 3\theta + T_2 \sin 5\theta + \dots T_{N-1} \sin (2\pi - \theta) = 0,$$

$$T_N \cos \theta + T_1 \cos 3\theta + T_2 \cos 5\theta + \dots T_{N-1} \cos (2\pi - \theta) = -P.$$

By the same process as in the case of $\phi = 0$ we find

$$V_0' = P/2. \quad \dots \dots \dots (20)$$

Then, from equation (8) when $r=1$, we obtain

$$H_0'(4\theta \cos \theta \sin 2\theta) \\ = 4(m_0' + H_0')(1 - \cos 2\theta) + T_N(2\theta \cos 2\theta - \sin 2\theta) \\ - P\{\sin \theta + \theta \cos \theta(1 - 2 \cos 2\theta)\} \\ - \frac{1}{G}\{T_1 + T_N(1 - 2 \cos 2\theta)\}, \quad (21)$$

and from equation (10)

$$\frac{(m_0' + H_0')}{P} = \pi \left\{ 2(1 - \cos 2\theta) + G(2\theta + \sin 2\theta) \right\} - 2NG(1 - \cos 2\theta) \quad (22)$$

Thus, as before, the rim reactions are obtained in terms of the loads T_1 and T_N .

Even with the simplifications introduced by putting $\phi=0$ and $\phi=\theta$, however, the arithmetical work involved in an actual analysis is very complicated, and a wheel with six spokes represents the practical limit of the application of these methods. It was decided, therefore, following a suggestion by Professor R. V. Southwell, to attempt an approximate solution based upon an analysis of a wheel having an infinite number of spokes. In connexion with this analysis the authors have to express their appreciation of the interest and help given to them by one of their colleagues, Mr. J. Vint, M.A.

Wheel with an infinite number of spokes.—The case considered is that of a rim connected to a hub by a disk having peculiar elastic properties. The stress at any point must be purely radial, and the stress along any radius must be constant from the rim to the hub. The hypothetical disk will therefore increase in thickness from the rim to the hub in order to compensate for the decreasing circumferential length of a sector. Let fig. 3 represent such a wheel, having a radial load P applied at X' . The point X will be taken as the origin.

At any point on the rim at an angular distance ψ from X let

u = radial extension,

v = tangential movement,

Also let H = tangential force in the rim,

V = radial force,

M = bending moment,

the positive direction of these being as shown in fig. 3. Then we have*

$$H = -\frac{E_1 a}{R} \left(u + \frac{\partial v}{\partial \psi} \right), \quad \dots \quad (23)$$

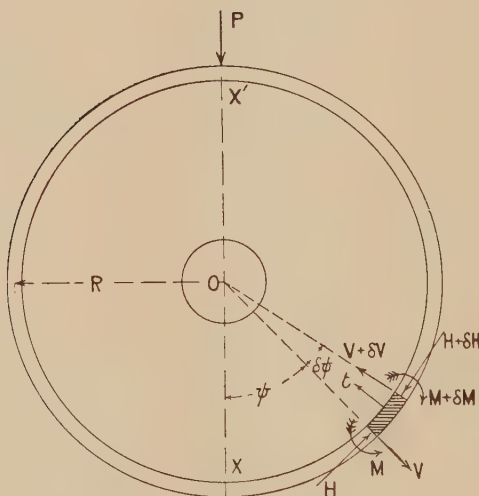
* H. Lamb, 'Dynamical Theory of Sound,' 2nd ed. p. 135.

$$M = \frac{E_1 I}{R^2} \left(\frac{\partial^2 u}{\partial \psi^2} + u \right), \quad . \quad . \quad . \quad (24)$$

where E_1 , I , R , and a have their usual significance.

If the intensity of inward radial pull from the disk upon the rim at the point considered is t per unit length of circumference, we obtain, by resolution of the forces

Fig. 3.



acting upon a small element of the rim as shown in the figure, the following relationships:—

$$\partial H / \partial \psi = -V, \quad . \quad . \quad . \quad (25)$$

$$\partial V / \partial \psi = H - tR, \quad . \quad . \quad . \quad (26)$$

$$\partial M / \partial \psi = VR. \quad . \quad . \quad . \quad (27)$$

Using equations (23) to (27) we obtain

$$\frac{\partial u}{\partial \psi} + 2 \frac{\partial^3 u}{\partial \psi^3} + \frac{\partial^5 u}{\partial \psi^5} + \frac{R^4}{E_1 I} \cdot \frac{\partial t}{\partial \psi} = 0.$$

Let Δ be the thickness of the disk at the rim, then

$$t = \frac{\Delta E_2 u}{L},$$

where L is the radial distance from hub to rim and E_2 is the modulus of elasticity for the disk. Putting

$$K = \frac{R^4}{E_1 I} \cdot \frac{\Delta E_2}{L},$$

the equation becomes

$$(1 + K) \frac{\partial^4 u}{\partial \psi^4} + 2 \frac{\partial^3 u}{\partial \psi^3} + \frac{\partial^5 u}{\partial \psi^5} = 0, \quad \dots \quad (28)$$

and the general solution is

$$u = A + B \sin \alpha \psi \sinh \beta \psi + C \cos \alpha \psi \cosh \beta \psi \\ + D \sin \alpha \psi \cosh \beta \psi + E \cos \alpha \psi \sinh \beta \psi,$$

where

$$\alpha = \sqrt{\frac{1}{2}\{(K+1)^{\frac{1}{2}}+1\}}, \quad \beta = \sqrt{\frac{1}{2}\{(K+1)^{\frac{1}{2}}-1\}},$$

and A, B, C, D , and E are constants of integration.

Since the solution must be symmetrical for equal positive and negative values of ψ between $\psi=0$ and $\pm\pi$, D and E will be zero, and the solution required is

$$u = A + B \sin \alpha \psi \sinh \beta \psi + C \cos \alpha \psi \cosh \beta \psi.$$

This satisfies the necessary conditions that

$$\frac{\partial u}{\partial \psi} = 0 \quad \text{and} \quad \frac{\partial M}{\partial \psi} = 0 \quad \text{when} \quad \psi = 0.$$

The three conditions required for the evaluation of the constants are:—

$$(1) \quad \frac{\partial u}{\partial \psi} = 0 \quad \text{when} \quad \psi = \pi.$$

(2) The total vertical force on the rim must be equal to the applied load, *i. e.*,

$$2 \int_0^\pi t R \cos \psi d\psi = P.$$

(3) In the analysis for the wheel with a finite number of spokes the compression strain-energy in the rim was neglected, *i. e.*, $1/aE$ was considered to be zero compared with R^2/EI , and so the same condition must be introduced in the present analysis.

Since

$$H = -\frac{aE}{R} \left(u + \frac{\partial v}{\partial \psi} \right),$$

$\left(u + \frac{\partial v}{\partial \psi}\right)$ must be put equal to zero if H is to be finite, and the third condition is thus

$$u = -\frac{\partial v}{\partial \psi}.$$

The first two conditions give

$$B = -\frac{PL}{2R\Delta E_2}$$

$$\sqrt{\frac{K}{K+1}} \left\{ \frac{\alpha \sin \alpha \pi \cosh \beta \pi - \beta \cos \alpha \pi \sinh \beta \pi}{\cosh^2 \beta \pi - \cos^2 \alpha \pi} \right\},$$

$$C = -\frac{PL}{2R\Delta E_2}$$

$$\sqrt{\frac{K}{K+1}} \left\{ \frac{\alpha \cos \alpha \pi \sinh \beta \pi + \beta \sin \alpha \pi \cosh \beta \pi}{\cosh^2 \beta \pi - \cos^2 \alpha \pi} \right\},$$

and the third gives upon integration

$$v = -A\psi - B \left\{ \frac{\beta \sin \alpha \psi \cosh \beta \psi - \alpha \cos \alpha \psi \sinh \beta \psi}{(\alpha^2 + \beta^2)} \right\} \\ - C \left\{ \frac{\beta \cos \alpha \psi \sinh \beta \psi + \alpha \sin \alpha \psi \cosh \beta \psi}{(\alpha^2 + \beta^2)} \right\} + F.$$

Since $v=0$ when $\psi=0$ the constant of integration $F=0$ also, $v=0$ when $\psi=\pi$, and so

$$A = \left(\frac{K}{K+1} \right) \frac{PL}{2\pi R\Delta E_2}.$$

Hence the complete solutions become

$$u = -\frac{PL}{2R\Delta E_2} \sqrt{\frac{K}{K+1}} \left[-\frac{1}{\pi} \sqrt{\frac{K}{K+1}} + C_1 \sin \alpha \psi \sinh \beta \psi \right. \\ \left. + C_2 \cos \alpha \psi \cosh \beta \psi \right], \quad (29)$$

$$t = -\frac{P}{2R} \sqrt{\frac{K}{K+1}} \left[-\frac{1}{\pi} \sqrt{\frac{K}{K+1}} + C_1 \sin \alpha \psi \sinh \beta \psi \right. \\ \left. + C_2 \cos \alpha \psi \cosh \beta \psi \right], \quad (30)$$

where

$$\left. \begin{aligned} C_1 &= \frac{\alpha \sin \alpha \pi \cosh \beta \pi - \beta \cos \alpha \pi \sinh \beta \pi}{\cosh^2 \beta \pi - \cos^2 \alpha \pi}, \\ C_2 &= \frac{\alpha \cos \alpha \pi \sinh \beta \pi + \beta \sin \alpha \pi \cosh \beta \pi}{\cosh^2 \beta \pi - \cos^2 \alpha \pi}. \end{aligned} \right\} \quad (31)$$

and

Then

$$M = \frac{E_1 I}{R^2} \left(\frac{\partial^2 u}{\partial \psi^2} + u \right) = - \frac{PR}{2\sqrt{K+1}} \left[C_1 \cos \alpha \psi \cosh \beta \psi - C_2 \sin \alpha \psi \sinh \beta \psi - \frac{1}{\pi \sqrt{K+1}} \right], \quad (32)$$

$$H = \frac{1}{R} \cdot \frac{\partial^2 M}{\partial \psi^2} + tR = \frac{P}{2\sqrt{K+1}} \left[C_1 \cos \alpha \psi \cosh \beta \psi - C_2 \sin \alpha \psi \sinh \beta \psi + \frac{K}{\pi \sqrt{K+1}} \right], \quad (33)$$

$$V = \frac{1}{R} \cdot \frac{\partial M}{\partial \psi} = - \frac{P}{2\sqrt{K+1}} \left[C_1 \{ \beta \cos \alpha \psi \sinh \beta \psi - \alpha \sin \alpha \psi \cosh \beta \psi \} - C_2 \{ \beta \sin \alpha \psi \cosh \beta \psi + \alpha \cos \alpha \psi \sinh \beta \psi \} \right]. \quad (34)$$

Adding (32) and (33), we get

$$(m + H) = \frac{P}{2\pi}.$$

When $\psi = \pi$, equations (33) and (34) give the reactions H_0 and V_0 of the previous analysis:—

$$H_0 = - \frac{P}{2\sqrt{K+1}} \left\{ \frac{\beta \sinh 2\beta\pi - \alpha \sin 2\alpha\pi}{\cosh 2\beta\pi - \cos 2\alpha\pi} - \frac{K}{\pi \sqrt{K+1}} \right\},$$

$$V_0 = \frac{P}{2},$$

and in the limiting case of a rigid rim when $K=0$ we obtain

$$H_0 = - \frac{P}{4\pi},$$

$$M_0 = \frac{3PR}{4\pi},$$

$$V_0 = \frac{P}{2},$$

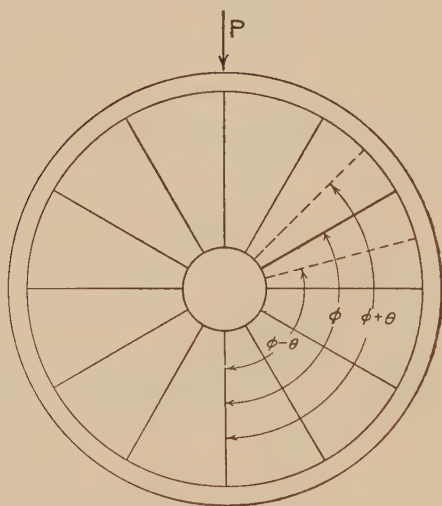
$$m_0 + H_0 = \frac{P}{2\pi}.$$

If we put $N=\infty$ and $2\theta=0$ in equations (19) we obtain the same values as above, showing agreement between the analyses in this limiting case.

Approximation for load in spokes.—The foregoing analysis of the case of an infinite number of spokes may be used to obtain an approximation to the loads in the spokes for a wheel where N is finite.

The total cross-sectional area of all the spokes in such a wheel is Na_0 , and if we imagine these replaced by a disk of the type just discussed, whose circumferential area at any radius is Na_0 , the thickness of this disk where it meets the rim will be $Na_0/2\pi R$.

Fig. 4.



Then, from our definition of K , we can write

$$K = \frac{R^4}{E_1 I} \cdot \frac{Na_0}{2\pi R} \cdot \frac{E_2}{L} = \frac{G}{\theta}, \quad \dots \quad (35)$$

where, as before, 2θ is the angle between adjacent spokes.

In fig. 4 let the origin be at the opposite end of the diameter to which P is applied, and let any spoke be ϕ from the origin. Then, if we assume that the load in this spoke is the same as that carried by the hypothetical disk between $(\phi + \theta)$ and $(\phi - \theta)$, we can write

$$T_\phi = R \int_{\psi=(\phi-\theta)}^{\psi=(\phi+\theta)} t d\psi.$$

Substituting for t from equation (30), we obtain as the load in the spoke

$$T_{\phi} = \frac{P}{N} \left(\frac{K}{K+1} \right) - \frac{P \sqrt{K}}{2(K+1)(\cosh^2 \beta \pi - \cos^2 \alpha \pi)} \\ \times [\{\cos \alpha(\pi + \phi) \sinh \beta(\pi - \phi) \\ + \cos \alpha(\pi - \phi) \sinh \beta(\pi + \phi)\} \\ \{\sqrt{K} \cos \alpha \theta \sinh \beta \theta + \sin \alpha \theta \cosh \beta \theta\} \\ + \{\sin \alpha(\pi + \phi) \cosh \beta(\pi - \phi) \\ + \sin \alpha(\pi - \phi) \cosh \beta(\pi + \phi)\} \\ \{\sqrt{K} \sin \alpha \theta \cosh \beta \theta - \cos \alpha \theta \sinh \beta \theta\}]. \quad (36)$$

Since the equation for t is valid only between $\psi=0$ and $\psi=\pm\pi$, this formula is not applicable either for T_N or for the spoke springing from the rim at $\psi=0$. For T_N we write

$$T_N = 2R \int_{\psi=\pi-\theta}^{\psi=\pi} t d\psi,$$

which on integration gives

$$T_N = -P \left(\frac{K}{K+1} \right) \left(\frac{N-1}{N} \right) + \frac{P \sqrt{K}}{2(K+1)} \cdot \frac{1}{\cosh^2 \beta \pi - \cos^2 \alpha \pi} \\ \{\sqrt{K}(\cos \alpha \theta \cosh \beta(2\pi - \theta) - \cos \alpha(2\pi - \theta) \cosh \beta \theta) \\ + \sin \alpha(2\pi - \theta) \sinh \beta \theta - \sin \alpha \theta \sinh \beta(2\pi - \theta)\} \quad (37)$$

Similarly, for the spoke springing from the point $\psi=0$,

$$T_0 = 2R \int_{\psi=0}^{\psi=\theta} t \cdot d\psi,$$

which leads to

$$T_0 = \frac{P}{N} \left(\frac{K}{K+1} \right) - \frac{P \sqrt{K}}{2(K+1)(\cosh^2 \beta \pi - \cos^2 \alpha \pi)} \\ [\sqrt{K}\{\cos \alpha(\pi - \theta) \cosh \beta(\pi + \theta) \\ - \cos \alpha(\pi + \theta) \cosh \beta(\pi - \theta)\} \\ + \{\sin \alpha(\pi + \theta) \sinh \beta(\pi - \theta) \\ - \sin \alpha(\pi - \theta) \sinh \beta(\pi + \theta)\}]. \quad (38)$$

In actual wheels K is so large that $\sinh 2\beta\pi$ is very nearly equal to $\cosh 2\beta\pi$, so that these equations can be simplified still further, and we obtain

$$T_N = P \left[-\frac{K}{K+1} \left(\frac{N-1}{N} \right) + \frac{\sqrt{K}}{K+1} \cdot e^{-\beta\theta} \{ \sqrt{K} \cos \alpha\theta - \sin \alpha\theta \} \right], \quad (39)$$

$$T_0 = P \left[\frac{K}{K+1} \left\{ \frac{1}{N} - e^{-\beta(\pi-\theta)} \cos \alpha(\pi-\theta) + e^{-\beta(\pi+\theta)} \cos \alpha(\pi+\theta) \right\} + \frac{\sqrt{K}}{K+1} \{ e^{-\beta(\pi-\theta)} \sin \alpha(\pi-\theta) - e^{-\beta(\pi+\theta)} \sin \alpha(\pi+\theta) \} \right]. \quad (40)$$

If, in addition to the above approximation, we write $(\pi-n\theta)$ for ϕ in equation (36), we obtain

$$T_{(\pi-n\theta)} = P \left[\frac{K}{K+1} \left\{ \frac{1}{N} - \frac{e^{(1-n)\beta\theta}}{2} (\cos(n-1)\alpha\theta - e^{-2\beta\theta} \cos(n+1)\alpha\theta) \right\} + \frac{\sqrt{K}}{2(K+1)} \cdot e^{(1-n)\beta\theta} \{ \sin(n-1)\alpha\theta - e^{-2\beta\theta} \sin(n+1)\alpha\theta \} \right]. \quad (41)$$

Equations (39) and (41) provide approximations for T_N and T_1 which enable solutions to be obtained for the two cases of symmetrical loading; thus:—

When $\phi=0$, T_N is given by equation (39). By putting $n=2$ in equation (41) we find

$$T_1 = P \left[\frac{K}{K+1} \left\{ \frac{1}{N} - \frac{e^{-\beta\theta}}{2} (\cos \alpha\theta - e^{-2\beta\theta} \cos 3\alpha\theta) \right\} + \frac{e^{-\beta\theta} \sqrt{K}}{2(K+1)} (\sin \alpha\theta - e^{-2\beta\theta} \sin 3\alpha\theta) \right]. \quad (42)$$

When $\phi=\theta$, T_N and T_1 are found by putting $n=1$ and $n=3$ in equation (41) to be

$$T_N = P \left[\frac{K}{K+1} \left\{ \frac{1}{N} - \frac{1}{2} (1 - e^{-2\beta\theta} \cos 2\alpha\theta) \right\} - \frac{\sqrt{K}}{2(K+1)} \cdot e^{-2\beta\theta} \sin 2\alpha\theta \right], \quad (43)$$

$$T_1 = P \left[\frac{K}{K+1} \left\{ \frac{1}{N} - \frac{e^{-2\beta\theta}}{2} (\cos 2\alpha\theta - e^{-2\beta\theta} \cos 4\alpha\theta) \right\} \right. \\ \left. + \frac{\sqrt{K}}{2(K+1)} \cdot e^{-2\beta\theta} \{ \sin 2\alpha\theta - e^{-2\beta\theta} \sin 4\alpha\theta \} \right]. \quad (44)$$

These approximate values of T_N and T_1 can be used in equations (15), (18), and (21) to evaluate the rim reactions, and the appropriate equations for T_r will then provide the loads in all spokes if these are required. In general, however, only certain maximum values of the loads and moments are needed.

In the first place, equation (39) gives the maximum compressive load which can occur in any spoke, and this is the minimum initial tension which must be given to all spokes to prevent them becoming inoperative under working conditions.

The greatest bending moment in the rim is also needed, and from an examination of calculations and curves in the second part of the paper it will be clear that this occurs when $\phi = \theta$ and is at the point of application of the load.

The maximum tensile load in a spoke is also required, and to determine this approximately we proceed as follows:—

Upon differentiating equation (30) with respect to ψ , and equating to zero for maximum and minimum values of t , we obtain the equation

$$\tan \alpha\pi \cot \alpha\psi = \tanh \beta\pi \coth \beta\psi,$$

which is satisfied when $\psi = 0$ and when $\psi = \pi$. Fig. 12 shows, however, that there is another value of ψ which satisfies this equation, this value being approximately 60° when $K=10$, and 135° when $K=1000$.

For all practical values of K we can write

$$\tanh \beta\pi \coth \beta\psi = 1 \quad \text{approximately,}$$

and the equation then becomes

$$\tan \alpha\pi = \tan \alpha\psi,$$

$$i. e., \quad \psi = \pi \quad \text{or} \quad \left(\frac{\alpha-1}{\alpha} \right) \pi.$$

The second value is the one required, and the curves of fig. 12 show that this gives the maximum tensile stress.

In general, for the load at a given point this value of ψ will not coincide with the position of a spoke, but since we

are only concerned with an approximation for a wheel where N is large, we shall assume that we can put

$$\phi = \left(\frac{\alpha - 1}{\alpha} \right) \pi \quad \text{in equation (36),}$$

$$\text{or} \quad (\pi - n\theta) = \left(\frac{\alpha - 1}{\alpha} \right) \pi \quad \text{in equation (41).}$$

Substituting $n = N/\alpha$ in equation (41), we obtain as the greatest tensile load in a spoke,

$$\begin{aligned} \frac{T_{\max.}}{P} = \frac{K}{K+1} \cdot \frac{1}{N} + \frac{e^{\beta(1-N/\alpha)\theta}}{2} \left\{ \frac{K}{K+1} (1 - e^{-2\beta\theta}) \cos \alpha\theta \right. \\ \left. + \frac{\sqrt{K}}{K+1} (1 + e^{-2\beta\theta}) \sin \alpha\theta \right\}. \quad (45) \end{aligned}$$

PART II.

Arithmetical Solutions of Certain Cases.

The analyses of Part I. will now be used to obtain complete arithmetical solutions for certain cases, partly to illustrate the behaviour of a spoked wheel and also for comparison with the experimental investigation to be described in Part 3.

Case I.—Wheel with three spokes.

In this case $2\theta = 2\pi/3$, and equations (2) and (3) give

$$T_2 = T_1 - P \sin \phi \operatorname{cosec} 2\theta,$$

$$T_3 = T_1 + P (\cot 2\theta \sin \phi - \cos \phi);$$

upon substituting these values in (5), (6), and (7), we obtain

$$(m_0 + H_0) = \frac{1}{2\pi} \left[P \left\{ 1 - \cos \phi - \frac{3 \sin \phi \operatorname{cosec} 2\theta}{2} \right\} + 3T_1 \right],$$

$$H_0 = P \left[\left(\frac{1}{3} - \frac{\phi}{2\pi} \right) \sin \phi \right] + \frac{T_1 \sin 2\theta}{3},$$

$$V_0 = P \left[\frac{1}{3} \sin \phi \cot 2\theta - \frac{\phi \cos \phi}{2\pi} \right] + \frac{T_1}{2}.$$

Putting $r=1$ in equation (8), and substituting the above values for $(m_0 + H_0)$, H_0 , V_0 , T_2 , and T_3 , we obtain

$$T_1 = \frac{P}{3} \left[\frac{\Phi G + \sqrt{3} \sin \phi + \cos \phi}{1 + 0.03188 G} \right],$$

where

$$\begin{aligned} \Phi = 0.95493 - (0.44481 + 0.28867 \phi) \sin \phi \\ - (0.95493 - 0.5 \phi) \cos \phi. \end{aligned}$$

The maximum value of T_1 occurs when $\phi = 60^\circ$ and is

$$T_1(\text{max.}) = \frac{P}{3} \left(\frac{0.09228 G + 2}{1 + 0.03188 G} \right).$$

When $\phi = 0$,

$$T_1 = \frac{P}{3} \left(\frac{1}{1 + 0.03188 G} \right).$$

TABLE I.

	$\phi = 0.$	$\phi = 60^\circ.$
T_1	$\frac{P}{3} \left(\frac{1}{1 + 0.03188 G} \right)$	$\frac{P}{3} \left(\frac{0.09228 G + 2}{0.03188 G + 1} \right)$
T_2	T_1	$T_1 - P$
T_3	$T_1 - P$	$T_1 - P$
H_0	$\frac{T_1}{2\sqrt{3}}$	$\frac{1}{4\sqrt{3}} (P + 2T_1)$
V_0	$\frac{T_1}{2}$	$\frac{1}{2} (T_1 - P/6)$
$m_0 + H_0$	$\frac{3T_1}{2\pi}$	$\frac{1}{2\pi} (3T_1 - P)$
m_0	$T_1 \left\{ \frac{3}{2\pi} - \frac{1}{2\sqrt{3}} \right\}$	$T_1 \left(\frac{3}{2\pi} - \frac{1}{2\sqrt{3}} \right) - P \left(\frac{1}{2\pi} + \frac{\sqrt{3}}{12} \right)$

The two cases $\phi = 0$ and $\phi = 60^\circ$ will be considered, and the values of the different terms are given in Table I.

Table II. gives the numerical values obtained from these results for various values of G . The variation of bending moment around the rim is shown in fig. 5 for two of the experimental wheels to be described in Part III.

TABLE II.

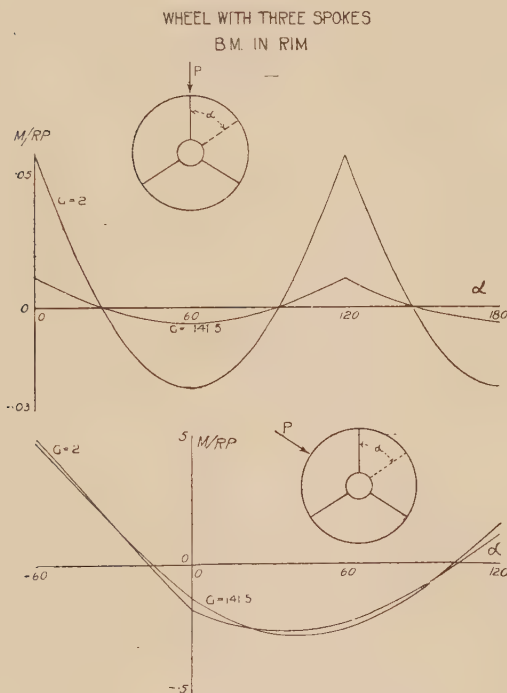
$\phi=0.$							$\phi=60^{\circ}.$								
G.	$T_1/P.$	$T_2/P.$	$T_3/P.$	$H_0/P.$	$V_0/P.$	$\frac{(m_0+H_0)}{P}$.	$m_0/P.$	G.	$T_1/P.$	$T_2/P.$	$T_3/P.$	$H_0/P.$	$V_0/P.$	$\frac{(m_0+H_0)}{P}$.	$m_0/P.$
0	0.333	0.333	-0.666	0.096	0.166	0.159	0.063	0	0.666	-0.333	-0.333	0.337	0.250	0.159	-0.178
1	0.323	0.323	-0.677	0.093	0.162	0.154	0.061	1	0.677	-0.323	-0.323	0.340	0.255	0.164	-0.176
5	0.287	0.287	-0.713	0.083	0.143	0.137	0.054	5	0.708	-0.292	-0.292	0.349	0.271	0.179	-0.170
10	0.253	0.253	-0.747	0.073	0.127	0.121	0.048	10	0.734	-0.266	-0.266	0.356	0.284	0.191	-0.165
20	0.203	0.203	-0.797	0.059	0.102	0.097	0.038	20	0.782	-0.218	-0.218	0.370	0.308	0.214	-0.156
30	0.170	0.170	-0.830	0.049	0.085	0.081	0.032	30	0.812	-0.188	-0.188	0.379	0.323	0.229	-0.150
40	0.146	0.146	-0.854	0.042	0.073	0.07	0.027	40	0.834	-0.166	-0.166	0.385	0.334	0.239	-0.146
50	0.128	0.128	-0.872	0.037	0.064	0.061	0.024	50	0.849	-0.151	-0.151	0.389	0.341	0.246	-0.143
80	0.094	0.094	-0.906	0.027	0.047	0.045	0.018	80	0.881	-0.119	-0.119	0.399	0.357	0.262	-0.137
100	0.080	0.080	-0.920	0.023	0.040	0.038	0.015	100	0.894	-0.106	-0.106	0.402	0.364	0.268	-0.134
200	0.045	0.045	-0.955	0.013	0.022	0.0215	0.0085	200	0.925	-0.075	-0.075	0.411	0.380	0.283	-0.128
300	0.032	0.032	-0.968	0.009	0.016	0.015	0.006	300	0.936	-0.064	-0.064	0.415	0.385	0.288	-0.127
400	0.024	0.024	-0.976	0.007	0.012	0.011	0.0045	400	0.942	-0.058	-0.058	0.416	0.390	0.291	-0.125
∞	0	0	-1.000	0	0	0	0	∞	0.966	-0.034	-0.034	0.423	0.400	0.302	-0.121

Case II.—Wheel with four spokes.

This wheel will only be considered for the case $\phi=0$ for comparison with experimental results. The static equilibrium conditions give

$$T_3 = T_1; \quad T_4 = T_2 - P.$$

Fig. 5.



Then, from equations (5), (6), and (7) we obtain

$$H_0 = T_1/2,$$

$$V_0 = T_2/2,$$

$$(m_0 + H_0) = \frac{2}{\pi} (H_0 + V_0) = \frac{T_1 + T_2}{\pi}.$$

Since $\phi=0$, we may use equation (16) to obtain relations between T_1 , T_2 , and the rim reactions, as follows:—

$$T_1 = -G \left[\frac{\pi H_0}{2} + V_0 - 2(m_0 + H_0) \right],$$

$$T_2 = -G \left[\pi V_0 - 4(m_0 + H_0) - G \left\{ \frac{\pi H_0}{2} + V_0 - 2(m_0 + H_0) \right\} \right] \\ - (2V_0 - P).$$

Combining these with the equations above, and solving the resulting simultaneous equations in H_0 and V_0 , we obtain

$$\frac{H_0}{P} = \frac{G \left(\frac{4}{\pi} - 1 \right)}{8 + 4G \left(\pi - \frac{8}{\pi} \right) + G^2 \left(\frac{\pi^2}{2} + \frac{16}{\pi} - 10 \right)},$$

$$\frac{V_0}{P} = \frac{2 - G \left(\frac{4}{\pi} - \frac{\pi}{2} \right)}{8 + 4G \left(\pi - \frac{8}{\pi} \right) + G^2 \left(\frac{\pi^2}{2} + \frac{16}{\pi} - 10 \right)},$$

TABLE III.

G.	H_0/P .	V_0/P .	$\frac{(m_0 + H_0)}{P}$.	m_0/P .	T_1, T_3 .	T_2 .	T_4 .
0	0	0.2500	0.1591	0.1591	0	0.5000	-0.5000
2	0.04256	0.2016	0.1561	0.1136	0.08491	0.4032	-0.5968
6	0.07042	0.1626	0.1516	0.0812	0.1408	0.3252	-0.6748
12	0.08083	0.1373	0.1389	0.0581	0.1617	0.2747	-0.7253
17	0.08223	0.1250	0.1319	0.0497	0.1645	0.2499	-0.7501
25	0.08050	0.1112	0.1221	0.0416	0.1610	0.2225	-0.7775
40	0.07403	0.09417	0.1071	0.0331	0.1481	0.1883	-0.8117
56.4	0.06684	0.08146	0.0944	0.0276	0.1337	0.1629	-0.8371
80	0.05812	0.06861	0.0807	0.0226	0.1162	0.1372	-0.8628
100	0.05218	0.06064	0.0718	0.0196	0.1044	0.1213	-0.8787
141.6	0.04293	0.04897	0.0585	0.0156	0.08586	0.09794	-0.9021

and a complete solution for the stress distribution is found.

The calculated values are given in Table III.

H_0 , T_1 , and T_3 are all zero, both when the rim is infinitely rigid, *i. e.*, when $G=0$, and also when the arms are infinitely rigid, *i. e.*, when $G=\infty$.

The maximum values occur when $G=17$; H_0 is then $0.0822P$ and $T_1=T_3=0.1645P$.

Case III.—Wheel with six spokes.

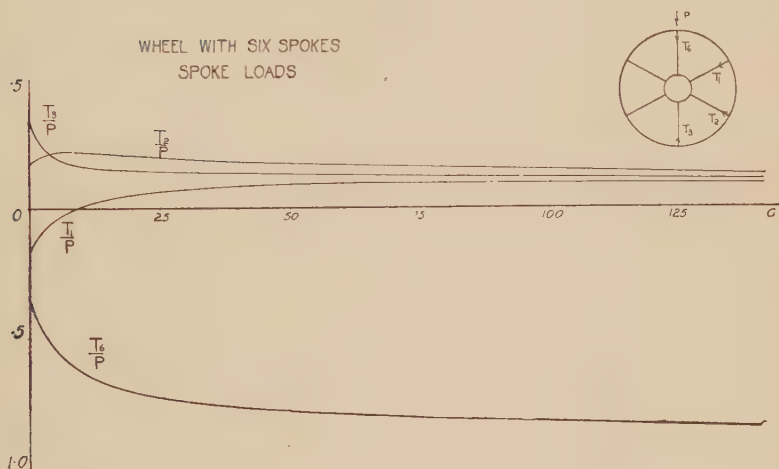
This case, which represents the practicable limit of the direct application of the equations on account of the arithmetical difficulties, was solved for $\phi=0$.

The calculations were carried out to ten significant figures, and were intended primarily as a standard solution for checking experimental results.

The reduction of the equations gave the following simultaneous equations:—

$$\begin{aligned}\alpha H_0 + \beta V_0 - \gamma(m_0 + H_0) &= \delta P, \\ \alpha' H_0 + \beta' V_0 - \gamma'(m_0 + H_0) &= \delta' P,\end{aligned}$$

Fig. 6.



where

$$\begin{aligned}\alpha &= 0.5378825320 G^2 - 6.2831853072 G - 6, \\ \beta &= 0.2030933255 G^2 - 5.0930906667 G + 1.7320508076, \\ \gamma &= 0.5930906667 G^2 - 8.6602540380 G, \\ \delta &= - 0.2965453335 G + 0.8660254038, \\ \alpha' &= 4.2736639193 G^2 - 6.2792720010 G, \\ \beta' &= 1.6136475960 G^2 - 18.8495559216 G - 18, \\ \gamma' &= 4.7123889804 G^2 - 18.0000000000 G, \\ \delta' &= - 2.3561944902 G - 6.\end{aligned}$$

Fig. 7.

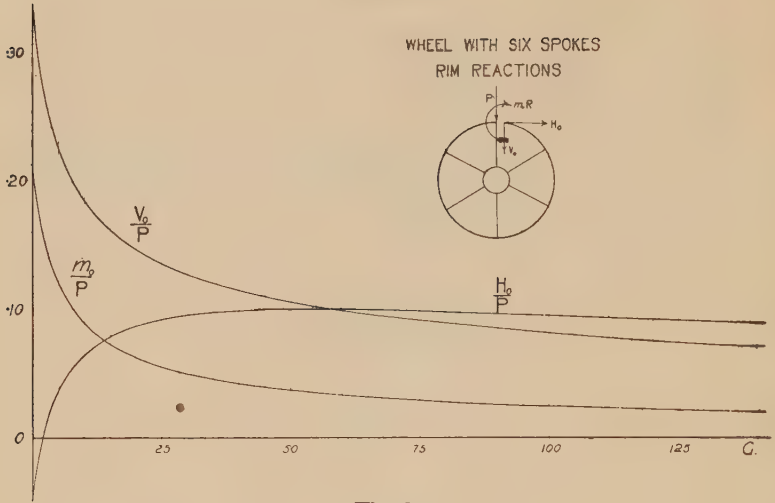
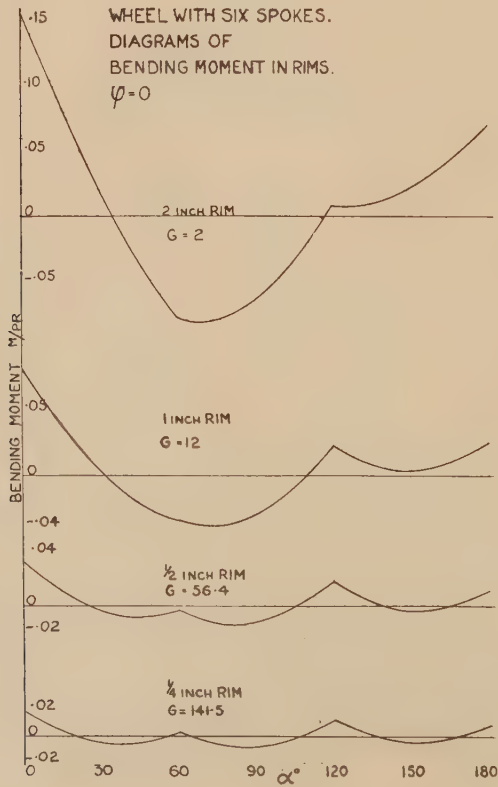


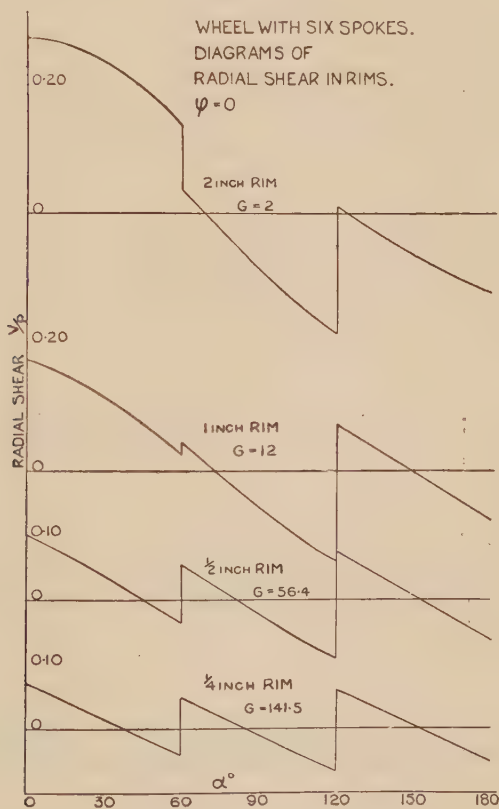
Fig. 8.



$(m_0 + H_0)$ can be calculated directly from equation (17), and H_0 and V_0 being found from the above, a complete solution is available.

The calculated values of the stresses are given to four significant figures in Table IV., and curves of spoke loads

Fig. 9.



and rim reactions are plotted in figs. 6 and 7. Bending moment, radial shear, and tangential force diagrams for the experimental rims are shown in figs. 8, 9, and 10.

The wheel with six spokes was also analysed for the case when $\phi = \theta$, i. e., when the load acts midway between the $(N-1)$ th and N th spoke. This was not done in so much detail as in the case $\phi = 0$, as it was only desired to verify the position of maximum bending moment in the rim.

TABLE IV.

Wheel with six spokes, $\phi=0$.

G.	$H_0/P.$	$V_0/P.$	$\frac{(m_0+H_0)}{P}.$	$m_0/P.$	$T_1, T_2.$	$T_2, T_3.$	$T_3.$	$T_6.$
0	-0.04811	0.3333	0.1591	0.2073	-0.1667	0.1667	0.3333	-0.3333
1	-0.01969	0.2981	0.1586	0.1783	-0.1275	0.1868	0.2818	-0.4038
2	0.00415	0.2726	0.1581	0.1577	-0.09866	0.1988	0.2478	-0.4547
4	0.02716	0.2377	0.1570	0.1299	-0.05832	0.2107	0.2064	-0.5245
6	0.04418	0.2144	0.1560	0.1118	-0.03055	0.2142	0.1841	-0.5712
8	0.05604	0.1975	0.1550	0.09894	-0.01026	0.2146	0.1700	-0.6051
10	0.06473	0.1844	0.1540	0.08923	0.003486	0.2133	0.1610	-0.6312
12	0.07135	0.1740	0.1530	0.08161	0.01799	0.2112	0.1548	-0.6520
20	0.08683	0.1465	0.1491	0.06227	0.05007	0.2006	0.1424	-0.7070
30	0.09507	0.1272	0.1445	0.04946	0.07010	0.1891	0.1353	-0.7457
40	0.09844	0.1148	0.1402	0.04179	0.08101	0.1790	0.1315	-0.7704
50	0.09957	0.1059	0.1362	0.03661	0.08714	0.1706	0.1283	-0.7882
56.4	0.09963	0.1014	0.1337	0.03407	0.08963	0.1659	0.1265	-0.7973
60	0.09951	0.09908	0.1324	0.03285	0.09067	0.1634	0.1254	-0.8018
80	0.09767	0.08893	0.1253	0.02767	0.09339	0.1516	0.1196	-0.8221
100	0.09482	0.08149	0.1190	0.02420	0.09336	0.1417	0.1146	-0.8370
141.5	0.08816	0.0704	0.1077	0.01958	0.08986	0.1257	0.1050	-0.8692

The rim bending moments for the four wheels used in experiments described in Part III. are given in Table V. both at the N th spoke ($m_0 R$) and under the load ($m_0' R$).

Fig. 10.

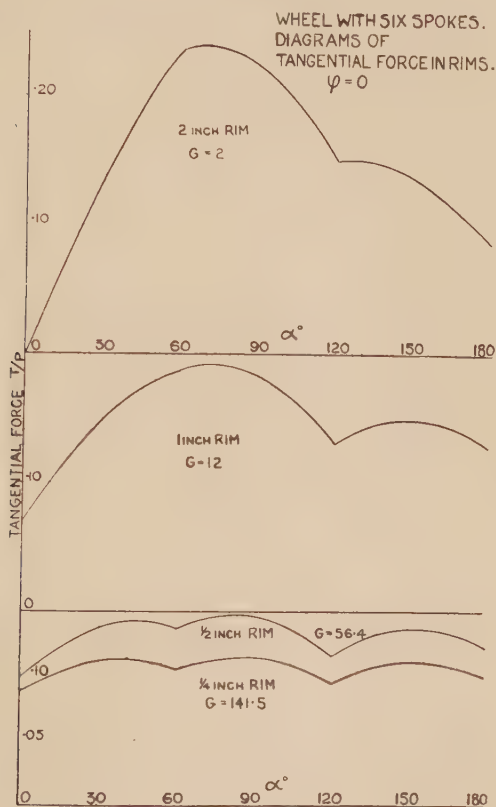


TABLE V.

Six-spoke Wheel when $\phi = 30^\circ$.

G .	$(m_0 + H_0)$.	H_0 .	V_0 .	m_0 .	m_0' .
2	0.1601	0.1879	0.1342	-0.0278	0.2318
12	0.1645	0.2197	0.0562	-0.0552	0.1995
56.4	0.1812	0.2480	0.0270	-0.0668	0.1835
141.5	0.2038	0.2714	0.0304	-0.0676	0.1791

Fig. 11.

WHEEL WITH SIX SPOKES
B.M. DIAGRAMS FOR
RIMS

$$\phi = \theta = 30^\circ$$

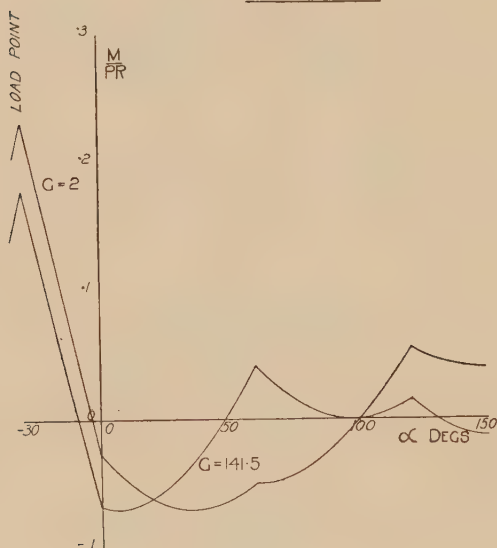


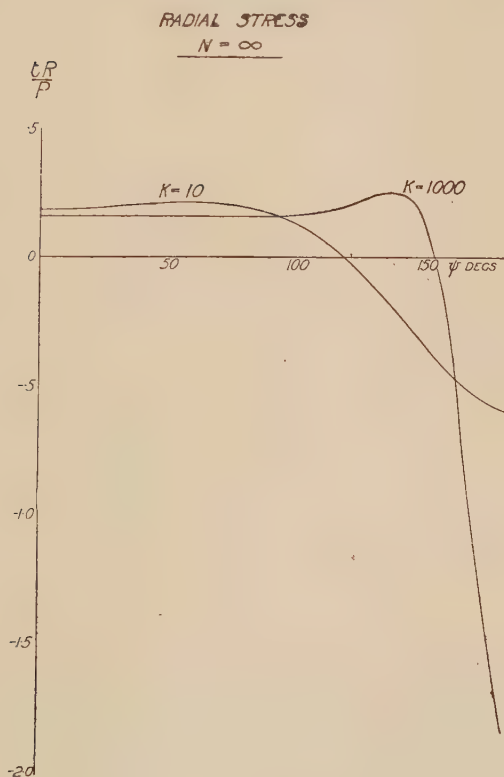
TABLE VI.
Variation of t round rim $N = \infty$.

Ψ degrees.	tR/P .	
	$K=10$.	$K=1000$.
0	0.1840	0.1592
15	0.1873	0.1592
30	0.1971	0.1593
45	0.2077	0.1593
60	0.2122	0.1593
90	0.1625	0.1557
120	-0.0297	0.2035
130	-0.1301	0.2443
140	-0.2437	0.2441
150	-0.3624	0.0792
160	-0.4737	-0.4151
170	-0.5563	-1.2587
180	-0.6032	-1.8626

It will be seen that m_0' is always greater than m , and is also greater than m_0 for the same rim when $\phi=0$.

Fig. 11 shows the variation of bending moment round the rims for the two extreme experimental wheels, viz., $G=2$ and $G=141.5$, and it is evident that $m_0'R$ is the maximum bending moment anywhere in the rim.

Fig. 12.



Case IV.—Wheel when N is infinite.

Two cases were calculated from the formulæ for the wheel with an infinite number of spokes, the values of K being 10 and 1000 respectively.

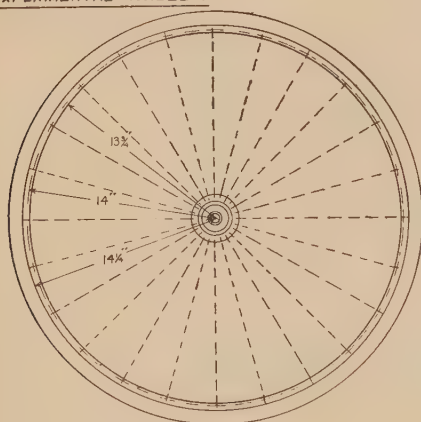
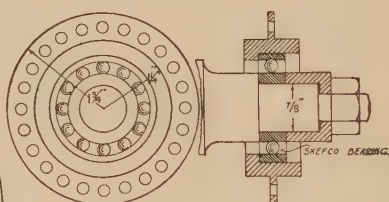
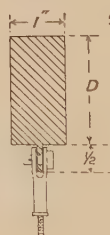
The variation of t around the rim is shown in fig. 12, the values being given in Table VI.

PART III.

Experimental Investigation.

The experimental investigation described in this section of the paper was undertaken with a twofold object. In the first place, it was felt to be desirable to check the mathematical analysis of Part I., and, secondly, it was necessary to extend the range of results beyond the practicable limit of calculation, so that the validity of the suggested approximate formulæ might be investigated.

Fig. 13.

EXPERIMENTAL WHEELS.DETAIL OF HUB.DETAIL OF RIM.

RIM	Nº 1	D = 1/4"
RIM	Nº 2	D = 1/2"
RIM	Nº 3	D = 1"
RIM	Nº 4	D = 2"

Special wheels were designed for this investigation, which are shown in fig. 13 and Pl. IV. The rims, four in number, were cut out of solid steel plate, so that the possibility of distortion and variation in elastic properties due to welding was avoided.

These rims were all made to a nominal thickness of 1 in., and their depths were nominally $\frac{1}{4}$, $\frac{1}{2}$, 1, and 2 in. respectively; these sizes give a wide range of rim stiffness.

The actual dimensions of the finished rims varied slightly from the nominal, and while, for ease of reference, these latter have been retained to distinguish the different rims, all calculations have been based upon the real dimensions, which are given in Table VII.

The hub, used for all the wheels, is illustrated in fig. 13, and is of simple design. It is turned out of solid bar steel and carries a self-aligning Skefco ball-bearing, so that when mounted on its shaft it can assume a vertical position independent of the setting of this shaft.

Two sizes of spokes were used: 4.B.A. steel rods and $\frac{1}{4}$ in. silver steel bars. The first were standard swaged rods to B.E.S.A. specification, and were attached to the flanges of the rims and hub of the wheels by standard fork-ends and pins; this gave pin-jointed ends in the plane of the wheel, as required by the assumptions of the analysis. The $\frac{1}{4}$ -in. bars were stock material, and the ends were turned down and screwed to fit the 4.B.A. fork-ends, in order to keep the end fittings as small as possible. Unless this had been done

TABLE VII.

Rim. in.	R. in.	Rim width. in.	Rim depth. in.	Flange thickness. in.	Flange depth. in.	I. in. units.
$\frac{1}{4}$	14.326	1.000	0.277	0.109	0.474	0.0089
$\frac{1}{2}$	14.45	0.9985	0.502	0.1086	0.477	0.02284
1	14.718	0.995	1.007	0.104	0.489	0.1136
2	15.228	1.000	2.005	0.107	0.488	0.7514

it would have been impossible to attach the required number of spokes to the hub.

The design of the rims and hub allowed wheels with 3, 4, 6, 12, and 24 spokes to be built up so that a good range of experimental work was possible.

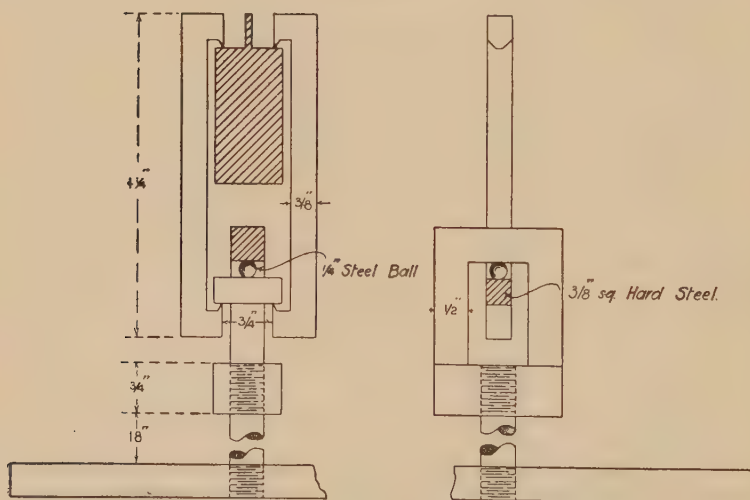
The wheel to be tested was erected on a simple three-armed jig, and every spoke was given an initial tension sufficient to ensure that it would remain taut under any load which was to be applied to the rim. It was then removed from the jig and mounted on a stub axle firmly attached to a large steel plate rag-bolted to a wall.

The device used for applying loads to the wheel is shown in fig. 14. It consists of two steel links with hardened knife edges, which rest in two small grooves scored on the inner edge of the rim equidistant from the mid-plane of the wheel. The knife edges at the other end of these links carry a small bridge-piece, in the centre of which a $\frac{1}{4}$ -in. steel ball rests.

The top bar of the load pillar rests on this ball. This device, coupled with the ball-bearing in the hub, ensures that loads placed on the pillar will be transmitted equally to each link and to a wheel hanging truly vertical, and that the line of action will pass through the centre of the wheel.

All strain measurements were made by Marten's extensometers of the mirror type. The gauge length was 5 in., and the strains were measured on opposite sides of a diameter, to eliminate errors due to non-axial load in a spoke. Fixed and moving mirrors were used, as it was found convenient to use two telescopes for reading the scale reflexions. The extensometer can be seen attached to a spoke in Pl. IV.

Fig. 14.



Preliminary Experiments.—The first experiments were carried out to determine the elastic properties of the wheels and spokes.

Determination of G.—Since

$$G = \frac{R^3}{E_1 I} \cdot \frac{a_0 E_2}{2L},$$

it was necessary to find $\frac{R^3}{EI}$ for the rim and $\frac{a_0 E}{L}$ for the spokes. If a circular rim be extended by equal and opposite

loads W acting at the ends of a diameter, the extension Δ is given by

$$\Delta = \frac{2WR^3}{EI} \left(\frac{\pi}{8} - \frac{1}{\pi} \right)^*.$$

Hence

$$\frac{R^3}{EI} = \frac{\Delta}{0.1488 W}.$$

Each rim, with the exception of the 2 in., was therefore hung on the stub axle and loads applied to the point diametrically opposite the support, through the load pillar previously described. Ames dial gauges reading to 0.0001 in. were mounted, to give the movement of the two ends of the diameter along which the load acted, and the value of Δ was thus obtained for a range of W . These gave excellent straight lines when plotted, the slope of which provided a direct evaluation of R^3/EI . The 2 in. rim was found to be too stiff for treatment in this way, but the value of E found from the other three rims was so consistent that it was possible to calculate R^3/EI for this rim with sufficient accuracy.

The next step was to find $a_0 E/L$ for the spokes, and this was done by means of a Marten's extensometer, in which the gauge-length was exactly the distance between the pin centres of the spoke when mounted in the wheel. The extensometer was actually fitted to the ends of the pins, so that the strain measured was that of the complete spoke, including turnbuckles and pins.

Since the extension $e = \frac{PL}{a_0 E}$, where E is the equivalent modulus for the spoke, $\frac{a_0 E}{L} = \frac{P}{e}$, and by plotting a range of measured extensions under varying direct tensile loads the term $a_0 E/L$ was evaluated.

This was done for a number of spokes, the mean value being taken for the calculation of G . Table VIII. gives the results of the experimental determination of G for the different rims.

Calibration of Spokes.—A number of spokes were calibrated so that strain measurements could be directly interpreted as loads in the spokes. The spoke to be calibrated was hung from a frame by a turnbuckle, as it would be attached to the rim of the experimental wheel, and loads

* Morley, 'Strength of Materials,' 7th ed. p. 407.

were applied to the other end. The Marten's extensometer to be used in the wheel experiments was mounted on the spoke, and a curve of extension against load thus obtained. From the curve a calibration constant was found, and such constant was used in all readings of strain for the particular spoke.

Accuracy of Experimental Results.—Throughout the experiments the gauge-length of the extensometer was 5 in., the width of the knife edges $\frac{3}{16}$ in., and the scale distance about 240 in. Hence the magnification given by the extensometer was about 2560, and using a 4.B.A. spoke, 1 mm. scale

TABLE VIII.
Experimental values of G.

Rim.	R^3/EI .	E. 10 ⁶ lb./sq. in.	$a_0 E/L$.		G.	
			4 B.A. spoke.	$\frac{1}{4}$ -in. spoke.	4 B.A. spoke.	$\frac{1}{4}$ -in. spoke.
in.						
$\frac{1}{4}$	0.01146	28.8	24,700	67,700	141.5	388
$\frac{1}{2}$	0.00457	28.9	"	"	56.4	155
1	0.000974	28.8	"	"	12.0	33
2	0.0001626	28.9	"	"	2.0	5.5

reading corresponded to approximately 0.75 lb. load in the spoke.

It was found that readings could be repeated to about 0.2 or 0.3 mm., and it was therefore considered reasonable to take the accuracy of experimental results as within ± 0.25 lb. for the 4.B.A. spokes, and within ± 1.5 lb. for the $\frac{1}{4}$ in. spokes.

These observational errors are independent of the size of the load measured, and when this load is small would appear very excessive if expressed as percentages.

It was decided therefore to express differences between experimental values and calculated values as absolute differences when comparing results obtained from the complete analysis for a finite value of N. This absolute difference is

$$P \left[\frac{T}{P} (\text{experimental}) - \frac{T}{P} (\text{calculated}) \right],$$

where P is the load applied in the experiment. In later experimental work, carried out to compare the agreement of results from approximate formulæ with those obtained by measurement, a percentage basis appeared to be a more satisfactory one to adopt, since discrepancies other than observational were to be expected.

It was decided therefore to express these differences as percentages upon the experimental values, and to indicate by an asterisk those in which the whole of the difference could be accounted for by observational errors of the amounts previously mentioned.

Experiments on Wheels.—Experiments were carried out on wheels having three, four, six, twelve, and twenty-four spokes, some of these being directly intended to verify the analysis and others to provide data for checking the legitimacy of the approximations described in Part I.

Most of the experiments were carried out with the load acting at a spoke point on the rim. This position, $\phi=0$, was a convenient one, and gave the required check of the analysis; but a number of tests were also carried out for $\phi=\theta$, and, in addition, the load in the spoke with maximum tension was measured in certain instances for comparison with equation (45).

In the analysis the load was assumed to act radially inward, as it would do in an actual wheel, but for ease of experimental work it was necessary to reverse the direction of loading. The only difference which this involves is in the signs of the spoke loads and rim reactions, and these have all been reversed in presenting the experimental work, to make them directly comparable with the analytical cases. A complete schedule of the experiments is given in Table IX.

The load applied to the rim was in all the experiments nominally 100 lb. The actual load, obtained by careful weighing of the added weights, was 98.33 lb., this value being used in reducing the experimental data.

Check of Analytical Work.—The three-, four-, and six-spoked wheel having been dealt with arithmetically in Part II. of the paper, experiments numbered 1–12 in the schedule were made for comparison purposes, and the results of these experiments are contained in Tables X., XI., and XII. These are discussed in Part IV.

Provision of Data.—Reference to Part I. will show that both for the case when $\phi=0$ and when $\phi=\theta$ the equations

TABLE IX.
Schedule of Experiments.

No.	No. of spokes.	Rim. in.	Spoke size.	G.	K = G/θ .	ϕ .	Loads measured.	Object.
1	3	$\frac{1}{4}$	4.B.A.	141.5	135	0	All spokes {	Check of analysis.
2	3	$\frac{1}{2}$	"	56.4	54	0	"	"
3	3	1	"	12.0	11.5	0	"	"
4	3	2	"	2.0	1.91	0	"	"
5	4	$\frac{1}{4}$	"	141.5	180	0	"	"
6	4	$\frac{1}{2}$	"	56.4	72	0	"	"
7	4	1	"	12.0	15.3	0	"	"
8	4	2	"	2.0	2.55	0	"	"
9	6	$\frac{1}{4}$	"	141.5	270	0	"	"
10	6	$\frac{1}{2}$	"	56.4	108	0	"	"
11	6	1	"	12.0	23	0	"	"
12	6	2	"	2.0	3.82	0	"	"
13	12	$\frac{1}{4}$	"	141.5	540	0	T_1 and T_N {	Provision of data.
14	12	$\frac{1}{2}$	"	56.4	215	0	"	"
15	12	1	"	12.0	46	0	"	"
16	12	2	"	2.0	7.64	0	"	"
17	24	$\frac{1}{4}$	"	141.5	1081	0	"	"
18	24	$\frac{1}{2}$	"	56.4	431	0	"	"
19	24	1	"	12.0	92	0	"	"
20	24	2	"	2.0	15.3	0	"	"
21	12	$\frac{1}{4}$	$\frac{1}{4}$ in.	388	1482	0	"	"
22	12	$\frac{1}{2}$	"	155	592	0	"	"
23	12	1	"	33	126	0	"	"
24	12	2	"	5.5	21	0	"	"
25	24	$\frac{1}{4}$	"	388	2964	0	"	"
26	24	$\frac{1}{2}$	"	155	1184	0	"	"
27	24	1	"	33	252	0	"	"
28	24	2	"	5.5	42	0	"	"
29	12	$\frac{1}{4}$	"	388	1482	θ	"	"
30	12	$\frac{1}{2}$	"	155	592	θ	"	"
31	12	1	"	33	126	θ	"	"
32	12	2	"	5.5	21	θ	"	"
33	24	$\frac{1}{4}$	"	388	2964	θ	"	"
34	24	$\frac{1}{2}$	"	155	1184	θ	"	"
35	24	1	"	33	252	θ	"	"
36	24	2	"	5.5	42	θ	"	"
37	24	$\frac{1}{4}$	"	388	2964	0	{ Max. tension	{ Comparison with (45).
38	24	$\frac{1}{2}$	"	155	1184	0	"	"
39	24	1	"	33	252	0	"	"
40	24	2	"	5.5	42	0	"	"

TABLE X.
Experiments on Wheels with three spokes.

Spoke.	1/4 in. rim.			1/2 in. rim.			1 in. rim.			2 in. rim.		
	T/P.		Absolute Difference, lb.	T/P.		Absolute Difference, lb.	T/P.		Absolute Difference, lb.	T/P.		Absolute Difference, lb.
	Experi-mental.	Calcu-lated.		Experi-mental.	Calcu-lated.		Experi-mental.	Calcu-lated.		Experi-mental.	Calcu-lated.	
1	0.0622	0.0605	+0.08	0.1228	0.1191	+0.18	0.2488	0.2411	+0.38	0.3130	0.3133	-0.01
2	0.0590	0.0605	-0.07	0.1230	0.1191	+0.19	0.2451	0.2411	+0.20	0.3122	0.3133	-0.05
3	-0.9472	-0.9395	+0.38	-0.8885	-0.8809	+0.38	-0.7595	-0.7589	+0.03	-0.6893	-0.6867	+0.13

TABLE XI.
Experiments on Wheels with four spokes.

Spoke.	1/4 in. rim.			1/2 in. rim.			1 in. rim.			2 in. rim.		
	T/P.		Absolute Difference. lb.	T/P.		Absolute Difference. lb.	T/P.		Absolute Difference. lb.	T/P.		Absolute Difference. lb.
	Experi- mental.	Calcu- lated.		Experi- mental.	Calcu- lated.		Experi- mental.	Calcu- lated.		Experi- mental.	Calcu- lated.	
1	0.0820	0.0859	+0.1	0.1359	0.1337	+0.11	0.1591	0.1617	-0.13	0.0788	0.0849	-0.30
3	0.0850	0.0859	-0.04	0.1341	0.1337	+0.02	0.1584	0.1617	-0.16	0.0795	0.0849	-0.26
2	0.0974	0.0979	-0.025	0.1629	0.1629	0.00	0.2776	0.2747	+0.14	0.4109	0.4032	+0.38
4	-0.0089	-0.0021	+0.33	-0.8398	-0.8371	+0.13	-0.7286	-0.7253	+0.16	-0.5971	-0.5968	+0.01

TABLE XII.

Experiments on Wheels with six spokes.

Spoke.	1/4 in. rim.			1/2 in. rim.			1 in. rim.			2 in. rim.		
	T/P.		Absolute Difference, lb.	T/P.		Absolute Difference, lb.	T/P.		Absolute Difference, lb.	T/P.		Absolute Difference, lb.
	Experi-mental.	Calcu-lated.		Experi-mental.	Calcu-lated.		Experi-mental.	Calcu-lated.		Experi-mental.	Calcu-lated.	
1	0.0875	0.0899	-0.19	0.0913	0.0896	+0.17	0.0108	0.0180	-0.71	-0.1070	-0.0987	+0.82
5	0.0931	0.0899	+0.25	0.0874	0.0896	-0.22	0.0112	0.0180	-0.67	-0.1065	-0.0987	+0.77
2	0.1244	0.1257	-0.10	0.1631	0.1659	-0.27	0.2122	0.2112	+0.10	0.1972	0.1988	-0.16
4	0.1272	0.1257	+0.12	0.1620	0.1659	-0.38	0.2131	0.2112	+0.19	0.1949	0.1988	-0.38
3	0.1055	0.1050	+0.04	0.1262	0.1265	-0.03	0.1542	0.1548	-0.06	0.2488	0.2478	+0.10
6	-0.0560	-0.0592	-0.25	-0.8002	-0.7973	+0.28	0.6496	0.6520	-0.24	-0.4552	-0.4547	+0.05

can be expressed in terms of T_1 and T_N , and the experiments numbered 13-36 inclusive were directed to obtain these values.

TABLE XIII.

Experiments on Wheels with 12 and 24 spokes.

+ signifies tension; - signifies compression.

Exper. no.	No. of spokes.	ϕ .	Rim. in.	Size of spokes.	G.	$K=G/\theta$.	T_N/P .	T_1/P .
13	12	0	$\frac{1}{4}$	4.B.A.	141.5	540	-0.7545	-0.0604
14	12	"	$\frac{1}{2}$	"	56.4	215	-0.6235	-0.1213
15	12	"	1	"	12.0	46	-0.4272	-0.1842
16	12	"	2	"	2.0	7.6	-0.2643	-0.1750
17	24	"	$\frac{1}{4}$	"	141.5	1081	-0.5017	-0.2131
18	24	"	$\frac{1}{2}$	"	56.4	431	-0.3907	-0.2207
19	24	"	1	"	12.0	92	-0.2560	-0.1892
20	24	"	2	"	2.0	15.3	-0.1553	-0.1346
21	12	"	$\frac{1}{4}$	$\frac{1}{4}$ in.	388	1482	-0.8410	-0.0071
22	12	"	$\frac{1}{2}$	"	155	592	-0.7346	-0.0561
23	12	"	1	"	33	126	-0.5301	-0.1472
24	12	"	2	"	5.5	21	-0.3292	-0.1798
25	24	"	$\frac{1}{4}$	"	388	2964	-0.6139	-0.1770
26	24	"	$\frac{1}{2}$	"	155	1184	-0.4890	-0.2090
27	24	"	1	"	33	252	-0.3309	-0.2101
28	24	"	2	"	5.5	42	-0.1948	-0.1552
29	12	0	$\frac{1}{4}$	"	388	1482	-0.4876	+0.1723
30	12	"	$\frac{1}{2}$	"	155	592	-0.4698	+0.1204
31	12	"	1	"	33	126	-0.3933	+0.0252
32	12	"	2	"	5.5	21	-0.2773	-0.0729
3	24	"	$\frac{1}{4}$	"	388	2964	-0.4557	0
34	24	"	$\frac{1}{2}$	"	155	1184	-0.3937	-0.0701
35	24	"	1	"	33	252	-0.2909	-0.1270
36	24	"	2	"	5.5	42	-0.1833	-0.1230

By substituting them in the equations, complete solutions for the twelve and twenty-four spoke case can then be obtained, and these solutions will later be used for a discussion of the approximations given by equations (39), (42), (43), and (44).

The results of the experiments are given in Table XIII. In each case the value of T_N is the average of several readings taken on different spokes, and T_1 is the mean of at least two readings. In all cases the divergence of readings, *i. e.*, difference between maximum and minimum readings, was within the prescribed limit laid down previously.

The maximum tension in a spoke is given approximately by equation (45), and experiments 37-40 were made to compare actual and calculated values. These results are given in Table XIV.

TABLE XIV.

Comparison of Calculated and Measured Maximum Tension in a spoke.

Exp. No.	No. of spokes.	Rim. in.	Size of spokes. in.	ϕ .	G.	K.	$\pi - \psi$ max. tension.	Max. tension/P.		
								Actual.	Calculated.	Error %.
37	24	$\frac{1}{4}$	$\frac{1}{4}$	0	388	2964	34°	0.0600	0.0678	+13.0*
38	24	$\frac{1}{2}$	„	0	155	1184	43°	0.0626	0.0649	+ 3.7*
39	24	1	„	0	33	252	62°	0.0574	0.0596	+ 3.8*
40	24	2	„	0	5.5	42	93°	0.0523	0.0554	+ 5.9*

* Whole of error can be accounted for by possible observational errors.

PART IV.

Discussion of Results.

The discussion of the results of the experimental investigation falls under two heads—the verification of the theoretical analysis and the justification of the suggested approximations for the case of a large number of spokes such as always occurs in practice.

Verification of the Analysis.—The experiments intended for this purpose were carried out on wheels with three, four, and six 4.B.A. spokes, and for each of these, four different rims were used, giving a range of G from 2 to 141.5.

The results are given in Tables X., XI, and XII.

As explained earlier, it may be misleading to express divergences between calculated and experimental values upon a percentage basis, since the error in reading the extensometer is independent of the strain measured; the differences have therefore been tabulated in absolute amounts.

For the three-spoked wheel, out of twelve spokes measured five showed differences from calculation less than 0.1 lb., four of the remainder differences between 0.1 and 0.2 lb., while the other three gave 0.38 lb. each.

In the case of the four-spoked wheels, six out of sixteen measurements agreed within 0.1 lb., six within the limits 0.1 and 0.2 lb., and only two gave differences greater than 0.3 lb., the maximum being 0.38.

For the six-spoked wheels, twenty-four spokes in all were measured. Four were less than 0.1 lb. different from calculated values, eight gave differences between 0.1 and 0.2 lb., six, differences between 0.2 and 0.3 lb. None were greater than 0.38 lb. with the exception of four spokes—two in the 1 in. rim and two in the 2 in. rim. The actual load in these spokes was very small, and difficulty was experienced, since the extensometer did not give sufficient magnification.

Hence, out of a total of fifty-two spokes compared experimentally with calculated values, the following figures were obtained :—

Errors less than 0.1 lb. occurred in 15 spokes.

Errors between 0.1 and 0.2 lb. occurred in 18 spokes.

Errors between 0.2 and 0.3 lb. " " 8 "

Errors between 0.3 and 0.4 lb. " " 7 "

Errors between 0.67 and 0.82 lb. " " 4 "

Summarizing the results in another way : if errors lying between ± 0.25 lb. are considered to be unavoidable, 38 of the 52 spokes gave exact agreement between calculation and measurement.

The accuracy of the analysis and also the methods of carrying out the experimental work may therefore be considered to be satisfactory.

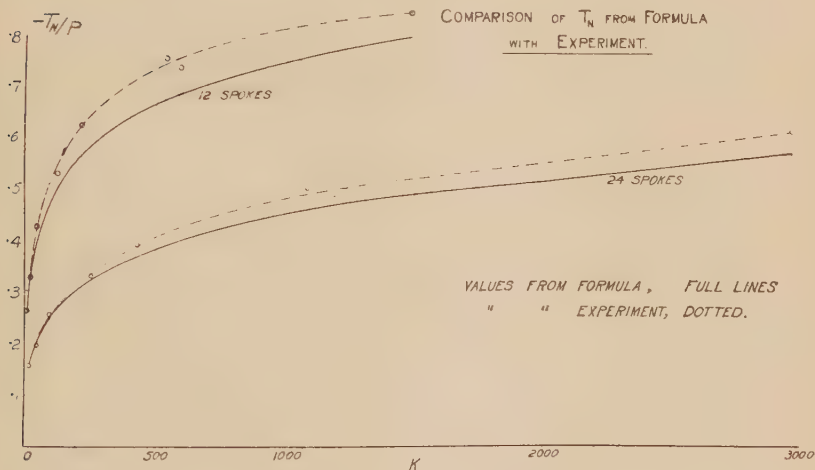
Justification of the Approximations for Use when N is Large.—The experiments made for this purpose may be conveniently discussed under three heads :—

- (1) Those made with the load at a spoke to determine T_1 and T_N .

- (2) Those made with the load midway between spokes to determine T_1 and T_N .
- (3) Those made to check the maximum tensile load in a spoke.

Experiments with $\phi=0$.—The experiments with the load at a spoke-point, *i. e.*, $\phi=0$, were made on wheels with twelve and twenty-four spokes, and since four rims were used and two different sets of spokes, eight experimental values of T_N and T_1 were obtained for each value of N . These experiments are numbered 13 to 28 in Table IX., and the results

Fig. 15.



are given in Table XIII. Having obtained values for T_N and T_1 , they were used to calculate the rim reactions from equations (15), (17), and (18), and the values thus obtained are given in the Tables XV. and XVI. as experimental values. Equations (39) and (42) were then used to obtain approximate values for T_N and T_1 , and hence the rim reactions by the use of the same equations as before. These are tabulated as calculated values. The results are exhibited graphically in fig. 15, where T_N is plotted against K . It will be seen that there is closer agreement for twenty-four than for twelve spokes between experiment and calculation. The value of T_N is the important term in this analysis, since it gives—for an inward radial force—the greatest compressive force in a spoke. It is thus a value below which the initial tensions in

TABLE XV.

Comparison of Results from Experiment and Approximate Formulæ for 12-spoke Wheels.

Case $\phi = 0$.

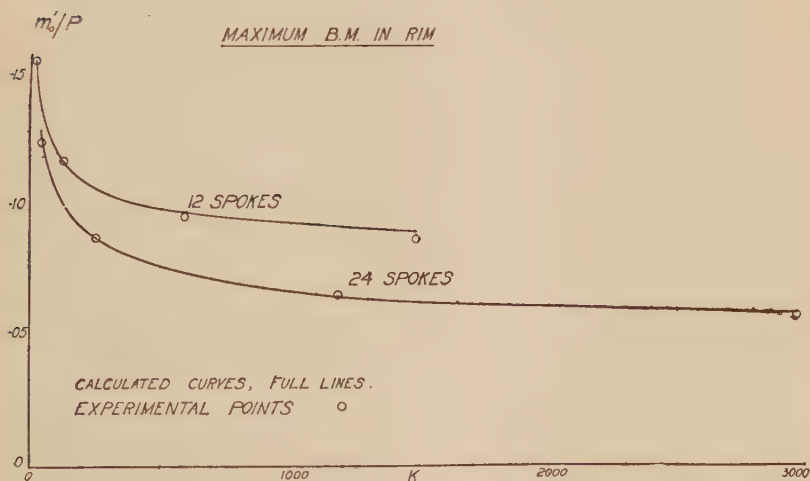
Exp. no.	K.	T _N /P.			T ₁ /P.			H _o /P.			V _o /P.			m _o /P.		
		Exp.	Calc.	Diff. %.	Exp.	Calc.	Diff. %.	Exp.	Calc.	Diff. %.	Exp.	Calc.	Diff. %.	Exp.	Calc.	Diff. %.
16	7.6	-0.2643	-0.2617	- 1.0*	-0.1750	-0.1746	-0.2*	-0.0056	-0.0023	-59.0	.3678	.3691	+0.4	.1646	.1613	-2.0
24	21	-0.3293	-0.3323	+ 1.1*	-0.1798	-0.1863	+3.6*	+0.0206	+0.0323	+ 9.1	.3354	.3336	-0.5	.1291	.1264	-2.1
15	46	-0.4272	-0.3995	- 6.5	-0.1842	-0.1841	0*	0.0518	0.0569	10.0	.2864	.3002	+4.8	.1063	.1012	-5.0
23	126	-0.5301	-0.5022	- 5.3	-0.1472	-0.1584	+7.6*	0.0811	0.0837	3.2	.2350	.2489	5.9	.0776	.0726	-6.4
14	215	-0.6235	-0.5668	- 9.1	-0.1213	-0.1329	9.6	0.0962	0.0952	- 1.0	.1882	.2166	15.0	.0582	.0591	+1.5
13	540	-0.7545	-0.6741	-10.6	-0.0604	-0.0713	18.0	0.1133	0.1083	- 4.4	.1227	.1629	33.3	.0344	.0393	14.2
22	592	-0.7346	-0.6855	- 6.7	-0.0561	-0.0641	14.3*	0.1123	0.1091	- 2.6	.1327	.1572	18.5	.0344	.0376	9.3
21	1482	-0.8410	-0.7963	- 5.3	-0.0071	+0.0080	- *	0.1131	0.1094	- 3.3	.0795	.1013	27.4	.0181	.0218	20.0

* Observational errors sufficient to account for these differences.

the spokes must not fall if they are to remain taut and operative in use.

The value of K for actual wheels was determined by calculating this quantity for a bicycle wheel and for two large aeroplane wheels. The bicycle wheel, having thirty-two spokes, has a value of $K=1400$. The two heavy wheels with eighty spokes have values of 226 and 95. It appears from this that the limits of practical values of K may be taken as 50 and 2000, and the curves of T_N show that within this range the approximate formulæ give good results for the twenty-four spoke wheel. As N increases, the approximation will increase in value, and it appears therefore that

Fig. 16.



for practical wheels the value of T_N thus found may be confidently used.

Experiments with $\phi = \theta$.—These experiments are numbered 29 to 36 in Table IX., and were made on wheels with twelve and twenty-four spokes. In this set of experiments, however, one size of spoke— $\frac{1}{4}$ in. diameter—only was used, since this gave a sufficient range of K to determine the validity of the approximations.

The importance of this case lies in the fact that the bending moment in the rim has its greatest value under the load when the load acts midway between spokes, and M_0' calculated from the experimental values of T_N and T_1 found for this

TABLE XVI.

Comparison of Results from Experiment and Approximate Formulæ for 24-spoke Wheels.

Case $\phi = 0$.

Exp. no	K.	T _s /P.			T ₁ /P.			H ₀ /P.			V ₀ /P.			m ₀ /P.		
		Exp.	Calc.	Diff. %	Exp.	Calc.	Diff. %	Exp.	Calc.	Diff. %	Exp.	Calc.	Diff. %	Exp.	Calc.	Diff. %
20	15.3	-0.1553	-0.1600	+3.0	-0.1346	-0.1389	+3.2	0.0091	0.0078	-14.3	.4223	.4200	-0.5	.1497	.1510	+1.0
28	42.0	-0.1948	-0.2066	5.7*	-0.1552	-0.1677	8.0*	0.0354	0.0389	+9.9	.4026	.3967	-1.5	.1229	.1194	-2.8
19	92	-0.2560	-0.2533	-1.05*	-0.1892	-0.1865	-1.4*	0.0540	0.0538	-0.4	.3720	.3733	+0.3	.1034	.1034	0
27	252	-0.3309	-0.3241	-2.05*	-0.2101	-0.2126	+1.2*	0.0765	0.0802	+4.8	.3345	.3389	1.0	.0775	.0737	-4.9
18	431	-0.3907	-0.3691	-5.5	-0.2207	-0.2191	-0.7*	0.0835	0.0876	4.9	.3046	.3154	3.5	.0669	.0628	-6.0
17	1081	-0.5017	-0.4584	-8.6	-0.2131	-0.2064	-3.1	0.0895	0.0913	2.0	.2491	.2708	8.7	.0491	.0476	-3.6
26	1184	-0.4890	-0.4679	-4.3	-0.2090	-0.2297	+5.1	0.0905	0.0935	3.3	.2555	.2660	4.1	.0467	.0437	-6.4
25	2984	-0.6139	-0.5718	-6.8	-0.1770	-0.1838	3.8*	0.0815	0.0845	0	.1930	.2141	10.0	.0322	.0322	0

* Observational errors sufficient to account for these differences.

case is the bending moment for which the rim would have to be designed.

The experimental values of T_1 and T_N are given in Table XIII., and are used in Tables XVII. and XVIII. to determine the experimental values of H_0' , V_0' , and m_0' . These are compared with the values calculated from the approximate formulæ for T_N and T_1 etc., and the curves of m_0' against K by calculation and experiment are given in fig. 16. It will be seen that the agreement is very good, especially for the 24-spoke wheel, and there appears to be no doubt that the approximation in this case can be relied upon to provide results of a high degree of accuracy.

Maximum Tension in a Spoke.—It has been shown in Part I. that under a radial compressive force on the rim the maximum tensile load in a spoke occurs at a position depending on the value of K , and an approximate formula for its magnitude is given in equation (45).

This value, added to the initial tension in the spoke, gives the actual load which every spoke in turn has to carry, and which would therefore constitute the design load.

Experiments 37 to 40 were therefore carried out as a check upon this formula, and the results are given in Table XIV.

Since the position of maximum tensile stress derived from the equations based on the assumption of an infinite number of spokes will not, in general, exactly coincide with the position of an actual spoke in a wheel where N is finite, it was not expected that such good agreement as in previous experiments would be obtained. It is evident, however, that the results justify the approximation when N is within the practical range. The error of 13 per cent. for the $\frac{1}{4}$ in. rim is probably due to the fact that the load was applied to a spoke-point and the spoke measured was 4° off the required position. It will be seen on reference to fig. 12 that as K increases the slope of the t -curve steepens, so that a small error in angle makes a bigger error in load.

Conclusion and Summary.

By the methods of strain energy analysis a complete solution of the problem of stress distribution in a radially spoked, radially loaded wire wheel is obtained. This solution, however, when the number of spokes exceeds six, is not by itself of great practical value, since the degree of accuracy required in arithmetical work renders it very long and

TABLE XVII.

12-spoke Wheel. $\phi = \theta$.

Exp. no.	K.	T _N /P.			T ₁ /P.			H ₀ /P.			m ₀ '/P.		
		Exp.	Calc.	Diff. %.	Exp.	Calc.	Diff. %.	Exp.	Calc.	Diff. %.	Exp.	Calc.	Diff. %.
32	21	-0.2773	-0.2885	+4.0*	-0.0729	-0.0767	+5.2*	0.0029	0.0027	-7.4	0.1574	0.1576	+0.2
31	126	-0.3993	-0.3854	-2.0*	+0.0252	+0.0131	-48.0*	0.0476	0.0180	+0.8	0.1184	0.1180	-0.3
30	592	-0.4698	-0.4434	-5.6	0.1204	0.0893	-26.0	0.0970	0.0953	-1.8	0.0969	0.0986	+1.8
29	1482	-0.4876	-0.4529	-7.1	0.1723	0.1195	-30.0	0.1716	0.1689	-1.6	0.0880	0.0908	3.2

* Observational errors sufficient to account for these differences.

TABLE XVIII.

24-spoke Wheel. $\phi = \theta$.

Exp. no.	K.	T _N /P.			T _I /P.			H ₀ /P.			m ₀ '/P.		
		Exp.	Calc.	Diff. %.	Exp.	Calc.	Diff. %.	Exp.	Calc.	Diff. %.	Exp.	Calc.	Diff. %.
36	42	-0.1833	-0.1958	+6.8*	-0.1230	-0.1309	+6.4*	0.0326	0.0280	-14.0	0.1257	0.1303	+3.6
35	252	-0.2909	-0.2907	0*	-0.1270	-0.1259	-0.9*	0.0656	0.0554	0	0.0888	0.0890	0
34	1184	-0.3937	-0.3850	-2.2*	-0.0701	-0.0851	+21.4*	0.0730	0.0735	+0.8	0.0662	0.0656	-0.9
33	2964	-0.4557	-0.4358	-4.4	-0	-0.0019	-	0.0601	0.0594	-1.2	0.0577	0.0584	+1.2

* Observational errors sufficient to account for these differences.

tedious in use. Sufficient experimental work has been done, however, to justify the use of approximate formulæ based on a mathematical analysis of the case of a wheel having an infinite number of spokes.

These approximations are good for the twenty-four-spoke wheel, and will increase in accuracy as the number of spokes increases.

So, for all wheels falling within the range of normal designs for this class of wheel, the following results may be used:—

When the load is at a spoke :

$$\begin{aligned}
 & (m_0 + H_0) \\
 & = P \left[\frac{1 - \cos 2\theta}{\pi \{ 2(1 - \cos 2\theta) + G(2\theta + \sin 2\theta) \} - 2NG(1 - \cos 2\theta)} \right], \\
 & V_0 = \frac{1}{2}(P + T_N), \\
 & H_0 = \frac{T_N \cos 2\theta - T_1}{G2\theta \sin 2\theta} + V_0(\cot 2\theta - 1/2\theta) + (m_0 + H_0) \frac{1 - \cos 2\theta}{\theta \sin 2\theta}, \\
 & T_N = -P \left[\left(\frac{K}{K+1} \right) \left(\frac{N-1}{N} \right) \right. \\
 & \quad \left. - \frac{\sqrt{K}}{K+1} \{ \sqrt{K} \cos \alpha\theta - \sin \alpha\theta \} e^{-\beta\theta} \right], \\
 & T_1 = P \left(\frac{K}{K+1} \right) \left[\frac{1}{N} - \frac{e^{-\beta\theta}}{2} \{ \cos \alpha\theta - e^{-2\beta\theta} \cos 3\alpha\theta \} \right] \\
 & \quad + \frac{Pe^{-\beta\theta} \sqrt{K}}{2(K+1)} (\sin \alpha\theta - e^{-2\beta\theta} \sin 3\alpha\theta),
 \end{aligned}$$

and T_N is the maximum compressive load which any spoke will have to carry. It is thus the minimum permissible initial tension to be given to all spokes.

When the load is midway between spokes :

$$\begin{aligned}
 & (m_0' + H_0') \\
 & = P \left[\frac{(1 - \cos 2\theta) + G(\theta - \sin \theta)(1 - \cos \theta)}{\pi \{ 2(1 - \cos 2\theta) + G(2\theta + \sin 2\theta) \} - 2NG(1 - \cos 2\theta)} \right], \\
 & V_0' = P/2, \\
 & H_0'(4\theta \cos \theta \sin 2\theta) \\
 & = 4(m_0' + H_0')(1 - \cos 2\theta) + T_N(2\theta \cos 2\theta - \sin 2\theta) \\
 & \quad - \frac{1}{G} [T_1 + T_N(1 - 2 \cos 2\theta)] \\
 & \quad - P[\sin \theta + \theta \cos \theta(1 - 2 \cos 2\theta)],
 \end{aligned}$$

$$T_N = P \left[\frac{K}{K+1} \left\{ \frac{1}{N} - \frac{1}{2} (1 - e^{-2\beta\theta} \cos 2\alpha\theta) \right\} - \frac{\sqrt{K}}{2(K+1)} \cdot e^{-2\beta\theta} \sin 2\alpha\theta \right],$$

$$T_1 = P \left[\frac{K}{K+1} \left\{ \frac{1}{N} - \frac{e^{-2\beta\theta}}{2} (\cos 2\alpha\theta - e^{-2\beta\theta} \cos 4\alpha\theta) \right\} + \frac{\sqrt{K}}{2(K+1)} \cdot e^{-2\beta\theta} (\sin 2\alpha\theta - e^{-2\beta\theta} \sin 4\alpha\theta) \right],$$

and $m_0'R$, obtained from these, is the maximum bending moment which can occur in the rim.

Maximum tension in a spoke.

The maximum tension in a spoke is approximately

$$P \left[\frac{K}{K+1} \cdot \frac{1}{N} + \frac{e^{\beta(1-N/\alpha)\theta}}{2} \left\{ \frac{K}{K+1} (1 - e^{-2\beta\theta}) \cos \alpha\theta + \frac{\sqrt{K}}{K+1} (1 + e^{-2\beta\theta}) \sin \alpha\theta \right\} \right],$$

which occurs at π/α from the load point.

In conclusion, the authors desire to express their thanks to the Aeronautical Research Committee for its financial assistance in carrying out the experimental work described and for permission to publish the results.

XXI. The Formation of Molecular Aggregates in Radon-Gas Mixtures containing Polar Molecules. By Prof. E. L. HARRINGTON, Ph.D., and O. A. GRATIAS*, M.Sc., University of Saskatchewan, Canada †.

SOME time ago one of the present writers ‡ reported evidence of the existence of aggregates of active deposit atoms in gases containing radon, and called attention to the important part apparently played by water vapour in the formation of the aggregates. Since it seemed probable

* Post-graduate student and holder of a bursary under the National Research Council of Canada.

† Communicated by the Authors.

‡ Harrington, Phil. Mag. vi. p. 685 (1928).

that the participation of the water molecules in the formation of the aggregates was due to their polar nature, it appeared desirable to determine whether other polar molecules might serve equally well in the process involved. With this object in mind a number of mixtures containing radon, air, and some vapour of polar molecules other than water vapour were studied by means of substantially the same experimental methods. The results obtained form the basis of the present report.

Methods employed.

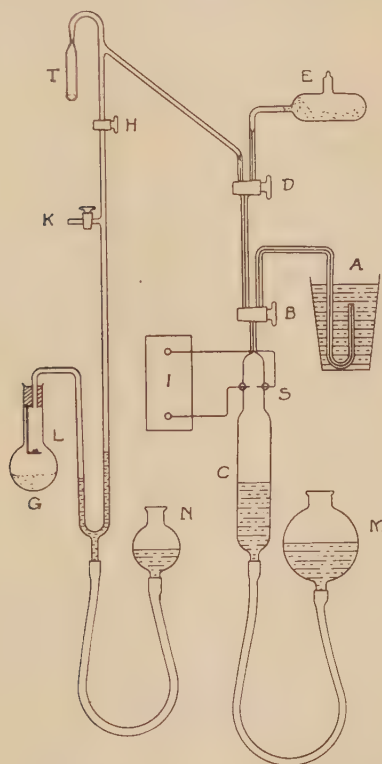
Inasmuch as the previous work was done in the Cavendish Laboratory*, and the present in the University of Saskatchewan, entirely different equipment was employed; but as there was no fundamental change in either the nature of the apparatus or the experimental procedure for the major portion of the work, a detailed description of the apparatus is not needed. Briefly stated, the work involved obtaining evidence of the presence of aggregates (1) by the centrifuge method, (2) by photographic means, and (3) through the use of the ultra-microscope. For the sake of checking, much of the previous work was repeated, and the results were found to be entirely consistent with those described in the first report. With this as a basis experiments involving polar molecules other than those of water vapour were undertaken. The procedure for each substance tested was much the same, except for the preparation and the introduction of the gas or vapour itself; hence the details for only one case, that of hydrogen chloride, will be given.

The essentials of the apparatus in simple form are shown in fig. 1. The radon-gaseous mixture as obtained from the radon pump system was transferred in the usual thimble mercury cup container to the mercury reservoir A. Through this it was introduced into the previously evacuated chamber C, where an electric spark at S caused the hydrogen and oxygen of the mixture to unite. In all cases where it was desired to remove the water vapour the remaining gaseous mixture was crowded into a drying-chamber E, and left until needed. The experimental tube, T, contained a small quantity of phosphorus pentoxide to take care of any residual water vapour. The hydrogen

* Under the direction of Sir Ernest Rutherford.

chloride generator G contained sulphuric acid and sodium chloride, the latter resting on a shelf, L. By lowering N and properly manipulating the stopcocks and M one could exhaust the generator and the other parts of the system as required. To obtain the gas it was necessary merely slightly to jar the generator so as to cause the salt to fall

Fig. 1.

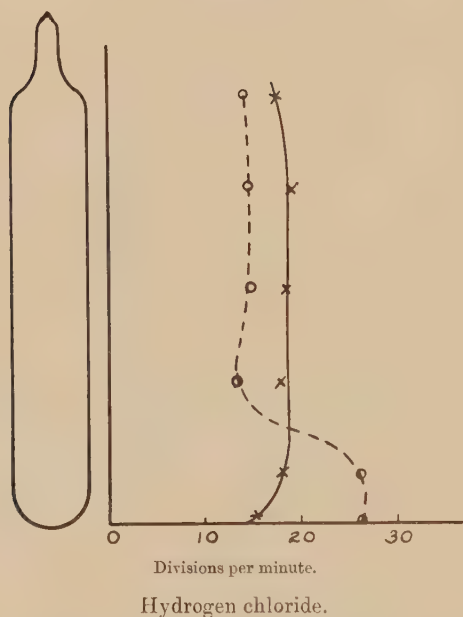


into the acid. The amount actually admitted to T was controlled by means of N. In practice the radon mixture from E and the dry gas from the generator were introduced into T together with sufficient dry air to bring the total pressure almost to that of the atmosphere, and finally the tube was tipped off by means of a blow torch.

The centrifuge method for examining for the presence of aggregates, fully described in the earlier paper, (*l. c.* p. 686

involved the following steps, briefly stated :—After allowing three or four hours for the aggregates to form, the distribution of activity along T was examined by means of a gamma-ray electroscope. To limit the radiation reaching the electroscope at one time to a short section of T two heavy lead blocks placed horizontally, the one above the other and separated from it by 1 centimetre, so as to form a virtual slit, were arranged between the electroscope and T. The rate of fall of the leaf for any position of T was

Fig. 2.



taken as a measure of the activity of the portion of T in front of the slit. By exposing different portions of T in turn data were obtained from which a curve representing the distribution of activity along the tube was plotted. Following this the tube was placed in a high-speed centrifuge, where it was centrifuged for a half-hour or more, and then a second distribution curve was taken in the same manner as before. In cases where the second curve showed a maximum in the portion corresponding to the end of the tube it was taken to mean that aggregates had been

Fig. 3.

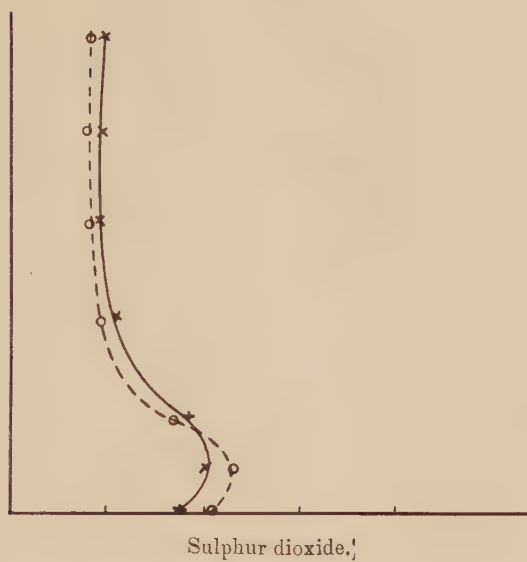


Fig. 4.

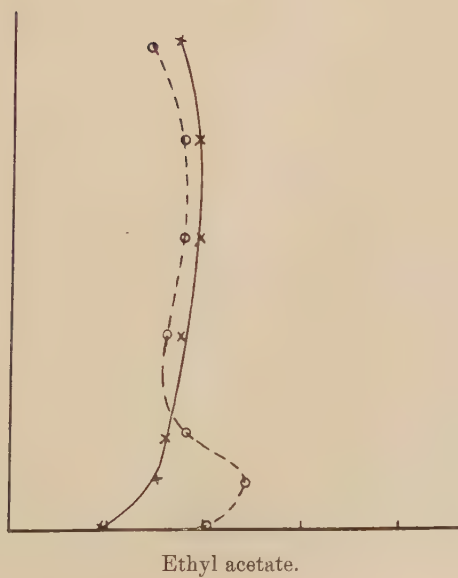


Fig. 5.

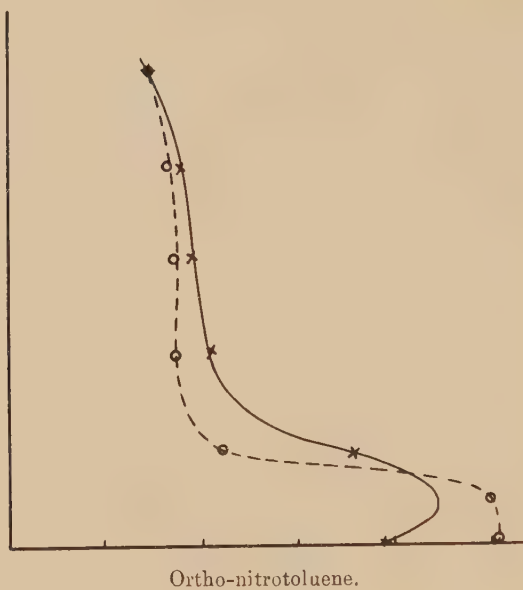
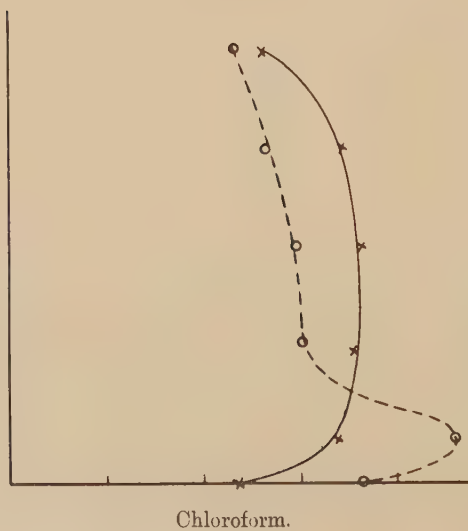
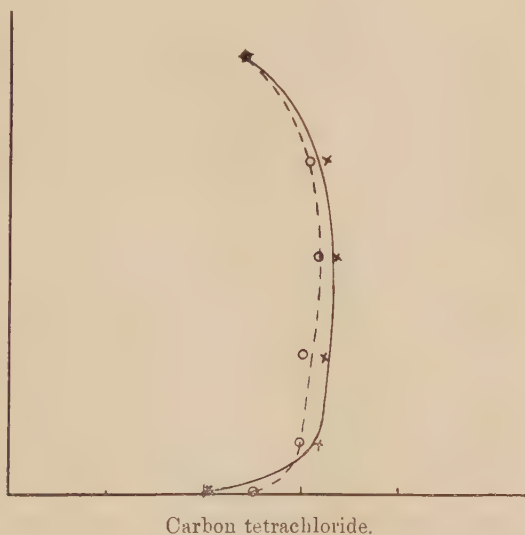


Fig. 6.



present and thrown to the end of T by the centrifugal force. The curves shown in figs. 2 to 7 will serve to illustrate the nature of the distribution curves. In each case the abscissae represent the activities of the corresponding portions of the tube as indicated in the case of fig. 2; in other words, the curves represent in every case the relation between the activities of 1 centimetre sections of the tube and their distances from the lower end, although the diagram for the tube is omitted in all except the one case.

Fig. 7.



Early in the work it was observed that the shape of the curve depended much upon the position in which the tube was left during the formation of the aggregates and prior to the observations before the tube was centrifuged. In cases where the tube was left horizontal the distribution of activity along the tubes was substantially uniform with the expected falling off in activity near the ends, but in cases where the tube was left vertical during the formation period even the curve taken prior to centrifuging showed a marked hump in the portion corresponding to the lower end of the tube. Figs. 3 and 5 show examples of the latter case. Subsequent to the discovery of this purely gravity effect curves of both types were taken for the various cases.

Cases in which large gravity effects were observed were in every instance cases which exhibited large effects from centrifuging, as would be expected, the large effects being due to conditions which especially favoured the growth of large aggregates. The marked effect of gravity is of course not a newly observed one, as it was early described by Mme Curie * and later by others.

In applying the second, or photographic, method of investigation several of the various methods as described by Mlle Chamié †, by Mühlestein ‡, by Harrington (*l. c.*), and by others were utilized, but the one usually employed involved placing a thin mica sheet within T, either as a lining or as a longitudinal partition, and exposing it directly to the radon mixture. After due time the mica was removed and pressed between two photographic plates for a few minutes. These plates were then developed in the usual manner, and finally examined under a microscope for the characteristic halos which indicate the presence of aggregates. While the results thus obtained served merely to check those obtained by the centrifuge method, two observations might be mentioned. In the first place the edges of the mica as well as the scratches were always much richer in aggregates than the smooth clean surfaces. That this edge effect could not be due merely to the scraping of the mica along the activated wall of the tube during its withdrawal was proven by the fact that the same richness was found around holes cut in the middle portion of the mica sheets, where there could have been no contact with the walls of the tube. Such an effect was, however, to be expected in view of the results of Jedrzejowski §. Further evidence of the gravity effect was obtained also by the photographic method by having the tube T inclined at an angle of about 45° during the exposure of a longitudinal mica partition. Upon the development of the plates it was found that the plate which was exposed to the side of the mica sheet which faced up during its activation was much richer in halos than the other plate.

In employing the ultra-microscopic method the radon mixture was introduced into a suitably constructed cell

* Curie, 'Radioactivité.'

† Mlle C. Chamié, *C. R.* clxxxiv. p. 1243 (1927); *J. de Phys. et de Radium*, x. p. 44 (1929).

‡ Mühlestein, *Archives des Sciences* [5] iv. p. 38 (1922).

§ Jedrzejowski, *C. R.* clxxxviii. p. 1167 (1929).

sealed on to the apparatus in place of T. The experimental arrangement was similar to that described by Whytlaw-Gray *, and such that a highly intense beam of light was thrown through a narrow slit in one of the sides of the cell. The appearance of specks of light or tiny "stars" in Brownian and convection movements in the field of the observing microscope was taken as evidence of the presence of aggregates. The validity and significance of such evidence has been discussed by Harrington (*l. c.*). In this connexion it should be reported that this phase of the work led to the development of a method of determining the mobilities of these aggregates, an account of which will appear later †.

As was reported in the previous paper, it was not found possible to detect the presence of aggregates in mixtures of radon and dry air. Since the gases of the air are true gases and non-polar, it was decided to try, in addition to the polar vapours indicated elsewhere, a non-polar vapour, that of carbon tetrachloride being selected. The results are shown in fig. 7.

Results and Discussion.

The substances employed in this investigation were selected from those listed by Debye ‡ on the basis of their electric moments and their convenience as to preparation and suitability for use under the conditions of the experiment. On account of the similarity of the curves obtained only typical ones have been reproduced. While one should hesitate to make any sweeping statements on the basis of the results of the nine polar substances which were tried, it is considered significant that in every case tried positive evidence of the formation of aggregates was obtained. The question as to whether some other polar substance might fail to give such evidence must, of course, remain unanswered.

From the very nature of things it is to be expected that the form of the curves would vary from substance to substance, and also among observations made with the same substance, for it is impossible to control with precision all of the factors involved, such as vapour density, radon strength, nature of the tube surfaces, freedom from dust or

* Whytlaw-Gray, Proc. Roy. Soc. cii. p. 600 (1923).

† In 'Canadian Journal of Research.'

‡ Debye, 'Polar Molecules.'

other impurities, etc. By an inspection of the curves shown it would appear that the effect with hydrogen chloride might be taken as of average magnitude, that with sulphur dioxide smaller, and that with orthonitrotoluene greater than the average. Relative to the substances for which curves are not shown it may be stated that in the case of methyl acetate the magnitude of the effect was slightly greater than, and the effect in acetone approximately the same as, the effect in ethyl acetate. The effect with paranitrotoluene was approximately the same as that shown for chloroform. It was not found possible with the amount of data available definitely to establish a correlation between the magnitude of the effect and that of the electric moment of the polar molecule employed.

Fig. 7 would indicate that no aggregates are formed when the non-polar vapour of carbon tetrachloride is employed in place of the polar substances above mentioned. This observation, taken with the similar results obtained when using the non-polar gases of the air, would at least suggest the conclusion that non-polar molecules do not favour the formation of molecular aggregates, although there may be, of course, non-polar molecules not as yet examined which might participate in such processes.

In the previous paper suggestions were offered as to conditions or processes involved in the growth of molecular aggregates in gases containing atoms of radioactive material, and the present results are quite in line with the ideas there expressed. A more exhaustive treatment of the basic principles involved has been given by Gibbs*, by Langmuir*, as well as by others. It would appear that in a mixture of radon and polar molecules the conditions are ideal for the formation of aggregates. It is believed that the presence of ions supplies the need of having nuclei for the formation of aggregates, and that the process is greatly facilitated when ions of both signs are present, as in the present case. Moreover, the electric field about an ion is exceedingly intense compared to the field about a molecule, even in the case of a strongly polar molecule. Since the radon molecules are mixed with the other molecules, not only are the beta and gamma rays effective, but the alpha rays especially so, with the result that the mixture is in a most highly ionized state. But this degree of ionization would exist whether the gases

* Alexander, 'Colloid Chemistry,' i. ; Gibbs, p. 393 ; Langmuir, p. 525.

or vapours associated with the radon were non-polar or polar: so the peculiar properties of polar molecules must be of importance. When ions of unlike sign from non-polar molecules are drawn together, there is no reason why one should expect them to remain together after they, through combination, have ceased to be ionic in character, for the disrupting effects of thermal agitations would more than overcome the binding forces, inasmuch as the electric field about a non-polar molecule is extremely small and falls off rapidly with distance. Except when non-polar molecules are ionized the field about them is essentially symmetrical, so there is no directive force operating to cause such molecules to make impacts on nuclei favouring permanent attachments. But with polar molecules it is quite otherwise; in such molecules the centre of gravity of the electrons does not coincide with that of the positive charges, and there results an external electrical field of an intensity depending on the separation of these centres. Moreover, the centre of mass in the case of polar molecules is likely to be far "off centre" with respect to the space that might at any instant be assigned to the molecule. This would obviously facilitate the orientation of the molecules, and coupled with the intense electric fields about polar molecules would greatly increase the probability of such molecules, like arrows, striking an aggregate in such a way as to stick. Quoting Langmuir (*l. c.*), "Such orientation of the polar molecules in the field of neighbouring molecules, if it occurs to any large degree, causes a very great increase in the attractive force between the molecules." It would seem then that the presence of such orientated layers of molecules about the nuclei of aggregates, whether such nuclei be dust particles or of ionic origin, would contribute to the aggregate not only through their own presence, but also through the resulting increased chance of other ions and polar molecules becoming added. That they do not leave the aggregate by evaporation is without doubt due to the lower vapour pressure possessed by molecules when thus orientated and packed. Mlle. Chamié has obtained experimental evidence that aggregates are exceedingly stable. It would therefore seem probable that an aggregate once formed would continue to grow until removed from the body of the gas through the action of gravity or through becoming attached to the walls of the containing vessel.

The exact part played by radon itself and its active deposits cannot be stated with certainty, but that it is important is seen from the fact that the magnitudes of the effects experimentally observed were found to increase with the richness of the mixture with respect to its radon content. This may be due in part to the corresponding increase in the degree of ionization of the mixture, but it is certainly due in large measure to such atoms becoming a part of the aggregate itself, as the evidence obtained in both the centrifuge and the photographic methods, as well as all the evidence obtained by other observers, points to the existence of aggregates of radioactive atoms. Since a single photographic plate will show halos varying through wide extremes in the number of atoms indicated as present in the various aggregates, it is certain that such atoms must do more than merely form a nucleus on which polar molecules can build, and that they do actually continue to become attached during the growth of the aggregate. However, this is to be expected in view of the fact that the active deposit atoms would tend to remain in the solid state at ordinary temperatures. Also their high atomic weight, and therefore their relatively low velocities, greatly increase the probability of their mutual impacts resulting in physical union. On the other hand, the number of such atoms present in the mixture employed in this research compared with the number of other molecules present is so very small that the probable impacts between radioactive atoms alone is too small to make it likely that aggregates could grow to a size sufficiently large to be detected in these experiments before decaying into relatively non-active products or before becoming removed through adsorption—again illustrating the importance of the presence of polar molecules.

Summary.

By various methods gaseous mixtures containing radon and its decay products have been investigated for the presence of molecular aggregates. Since in every case studied aggregates were obtained when the mixture contained polar molecules, and since in no case were aggregates detected when only non-polar molecules were present, it would appear that polar molecules definitely favour and are possibly essential in the formation of large aggregates in gaseous mixtures containing radon.

July 1st, 1930.

XXII. *The Paramagnetism of Polychromates.* By FRANCIS W. GRAY, M.A., D.Sc., Senior Lecturer in Chemistry, Aberdeen University, and JOHN DAKERS, B.Sc. *

THE anomalously low paramagnetism of the compounds of sexavalent chromium, of septivalent manganese, and of trivalent ruthenium, rhodium, tungsten, and iridium presents one of the most important problems of magnetochemistry. In every one of these cases the seat of the paramagnetism is usually considered to be in the element mentioned—for example, chromium in the chromium compounds. The atomic paramagnetism of the element in question is obtained by calculating the paramagnetic molecular susceptibility of its compound, and correcting this for the diamagnetic susceptibility of the constituent atoms. The effect of the diamagnetic correction is, of course, to give for the required atomic paramagnetism a value higher than the experimental molecular susceptibility. The results obtained hitherto have all been too low to square with theory. For example, the calculated atomic paramagnetism for Cr^{+6} has been equivalent to 1.9 Weiss magnetons, whereas the lowest possible number is 8.6 whether we regard paramagnetism as due to orbital rotation or to subelectronic spin. Similar figures are shown by the other metals in the above series.

The calculation of the number of magnetons per atom of any substance involves a knowledge of the Curie constant for that substance. Now, as far as we know, these substances with anomalously low paramagnetism have a susceptibility independent of temperature, so that the term Curie constant is not applicable to them. It must be understood, then, that any rough calculations with regard to the number of magnetons are made merely by utilizing the experimental susceptibility and the ordinary temperature at which it is measured. Nevertheless it is of considerable interest to inquire to what extent the low atomic paramagnetisms fall short of the theoretical minimum, and to what extent any correction can be applied to raise them.

Of the values found hitherto for the atomic paramagnetism of Cr^{+6} that calculated by Weiss and Collet,

* Communicated by the Authors.

Compt. Rend. clxxviii. p. 2146 (1924), and clxxxi. p. 1057 (1925), may be taken as typical. They derived the value 63.3×10^{-6} from experiments on $K_2Cr_2O_7$. The smallest possible value according to theory would be about 628×10^{-6} . To obtain the value 63.3×10^{-6} the experimental paramagnetism has already been raised by means of the diamagnetic correction. Now, a serious difficulty encountered in working out the above calculation is the uncertainty of this correction, and the question arises whether it would be possible by using a larger correction to raise the atomic paramagnetic susceptibility by the extra amount still required. As the rise must be about 565×10^{-6} , the highest likely diamagnetism appears at first quite insufficient.

In the present research we have been studying the magnetic properties of chromium trioxide and certain chromates and polychromates. Our experimental results for K_2CrO_4 and $K_2Cr_3O_{10}$ agree very well with those estimated by L. A. Welo, *Phil. Mag.* vi. pp. 481-509 (1928). On the other hand, for CrO_3 our value is at any rate in approximate agreement with those for the chromates, whilst Welo's value is obviously far too high, the excess being doubtless due to impurity.

The substances examined by us, when tested by chemical analysis, showed a purity of a very high order, and the problem is discussed here by the method described in "Diamagnetism and Sub-Molecular Structure," Gray and Farquharson, *Phil. Mag.* x. pp. 191-216 (1930).

As explained in that paper, the most suitable submolecular structure usually involves a certain amount of surplus electrons which go to form valency bonds. The magnetism of these valency electrons has an important bearing upon the present problem.

With regard to purity of material, it must be acknowledged that an impurity may be present in an amount too small to affect chemical analysis and yet large enough to be discernible by magnetic means. Is it possible that chromates may some day be obtained of so exceedingly high a state of purity that they will behave as diamagnetics? On the other hand, if the small paramagnetism is due to impurity, then, as the paramagnetism varies according to the amount of chromium, though not strictly proportional, so also the impurity must vary roughly as the amount of chromium.

Among the chromates studied by us were four, the chemical analysis for which agreed with the formulæ



The first two substances were British Drug Houses A.R. chemicals, the third and fourth were prepared by ourselves. The second, $\text{K}_2\text{Cr}_2\text{O}_7$, was taken as the standard in the analysis. The agreement between the chemical analysis and the formula is not so close in the fourth substance as in the first and third; but, if we judged by chemical analysis alone, we should certainly choose the formula $\text{K}_2\text{Cr}_4\text{O}_{13}$ rather than that of the next higher polychromate, namely $\text{K}_2\text{Cr}_5\text{O}_{16}$. The percentages of Cr corresponding to $\text{K}_2\text{Cr}_4\text{O}_{13}$ and $\text{K}_2\text{Cr}_5\text{O}_{16}$ are 42.09 and 43.76 respectively, whereas the analysis gives values from 41.73 to 40.89. Our chemical analysis also agrees with the usual practice, which is to regard $\text{K}_2\text{Cr}_4\text{O}_{13}$ as the formula of the chromate of potassium of highest known complexity.

Whatever view of molecular structure is adopted, it is always necessary to apply a diamagnetic correction to the experimental value of paramagnetism in order to obtain the true paramagnetism.

In making this correction we have utilized the diamagnetic atomic values calculated by Pauling for certain ions, together with the interpolated values for other ions given in Gray and Farquharson's paper. In our endeavour to interpret experimental results we have tried various selections of ions. Of these trial structures we propose to discuss only three that seem of special interest. In the first two cases we adopt the usual view that the seat of the paramagnetism is in the chromium ion or core; in the third case we abandon this conception and look for the source in the chromium-oxygen homopolar bonds.

In the *first* case we regard the constituent ions as being Cr^{+6} , O^{-2} , K^{+1} , and Na^{+1} , the proportion being such as to maintain the molecule neutral. In these structures all the electrons are subatomic, and all the diamagnetism applicable as a correction is therefore subatomic.

In the *second* case we utilize the ions Cr^{+6} , O^{+2} , K^{+1} , and Na^{+1} , the oxygen ion selected here being the one which we have found most suitable in other studies. In this structure, if the molecules are to be neutral, electrons are required in addition to those going to form the ions. Here the diamagnetism applicable as a correction consists

of two parts—the part derived from the subatomic electrons and that due to the interatomic or surplus electrons which may be regarded as forming valency bonds.

In the *third* case we consider structures of the type used by Gray and Farquharson in the study of halogenates and perhalogenates, where an interchange of electrons and consequent fluctuation of angular momentum would cause a small paramagnetism to a greater extent in the more homopolar bonds and to a less extent in the more heteropolar, as described in the above-mentioned paper. It has been found that this method provides the best interpretation of experimental results.

In this discussion the following values of atomic diamagnetism are utilized:—

Cr^{+6} .	K^{+1} .	Na^{+1} .	O^{-2} .	O^0 .	O^{+2} .
6.6	16.7	4.2	12.6	7.19	4.09

All these numbers and those in the following tables have to be multiplied by 10^{-6} .

First Trial Structure.

TABLE I.

The constituent ions in this table are

Cr^{+6} , O^{-2} , K^{+1} , and Na^{+1} .

Subst.	Experimental mol. sus.	Sum of ionic values.	Calculated values of paramagnetism of Cr^{+6} .	
			Total.	Per Cr atom.
K_2CrO_4	0.0	-90.4	90.4	90.4
$\text{K}_2\text{Cr}_2\text{O}_7$	+54.0	-134.8	188.8	94.4
$\text{K}_2\text{Cr}_3\text{O}_{10}$	+95.0	-179.2	274.2	91.4
$\text{K}_2\text{Cr}_4\text{O}_{13}$	+193.0	-223.6	416.6	104.1
CrO_3	+41.0	-44.4	85.4	85.4
Na_2CrO_4	+19.4	-65.4	84.8	84.8

Our values for the atomic paramagnetic susceptibility of Cr^{+6} are considerably higher than that of Weiss and Collet, 63.3, although still too much below the theoretical

value for one Bohr magneton, namely, 628. The only way of raising the numbers would be by supposing a higher diamagnetism for the subatomic electrons. This could be got by raising the principal quantum numbers of the electrons. But any quantum numbers that would be of any use for our purpose would involve subatomic orbital states unlikely to exist in the solid condition. We are therefore compelled to attempt an explanation of the numbers as they appear in the above table.

The atomic paramagnetism of Cr^{+6} , 85, which is very near that shown both by CrO_3 and by Na_2CrO_4 , is equivalent to about 0.367 Bohr magneton. We recollect that Gerlach and Stern obtained $\frac{1}{3}$ of a Bohr magneton for thallium, and that an explanation was obtained on the basis of the theory of the splitting factor. There is an important difference, however, between the two cases. The atomic state assumed for thallium was a doublet one, whereas in the case of Cr^{+6} we are obliged to assume a state of odd multiplicity, and there is no single state of odd multiplicity that would explain our result. It is true that a mixture in the right proportion of atoms of two different singlet states, an S state and a P state, one giving no magnetons and the other giving one Bohr magneton, would yield the fraction required; but we do not offer this as a likely explanation.

Again, if we assume a grouping together of single magnetons, so as to give the resultant effect of fractions of a magneton, then we have to suppose a group of about 7 units.

The second trial structure shows greater promise of yielding an interpretation.

The advantage of the second trial structure is that a new type of diamagnetic correction is available owing to the presence of valency electrons. Judging from the valency diamagnetism usually encountered we should expect that the highest correction which we could apply would be about 5 per pair of valency electrons. This would give, as shown in Table II., a paramagnetism per Cr^{+6} atom of 96.36, 99.61, 96.4, and 108.99 for K_2CrO_4 , $\text{K}_2\text{Cr}_2\text{O}_7$, $\text{K}_2\text{Cr}_3\text{O}_{10}$, $\text{K}_2\text{Cr}_4\text{O}_{13}$ respectively, or an average of 100.34. This is higher than that obtained from the first trial structure, but still far below the theoretical minimum of 628. The value 100.34 is equivalent to about 0.4 of a Bohr magneton. Explanations suggest themselves similar

to those considered for the first trial structure: firstly, that we have a mixture of two singlet states, one giving no magnetons and the other giving one magneton, the proportion required being 3 of the first to 2 of the second; or, secondly, that we have a group effect, the group in this case requiring to consist of about 6 units.

Second Trial Structure.

TABLE II.

The constituent ions of this table are

Cr^{+6} , O^{+2} , K^{+1} , and Na^{+1} .

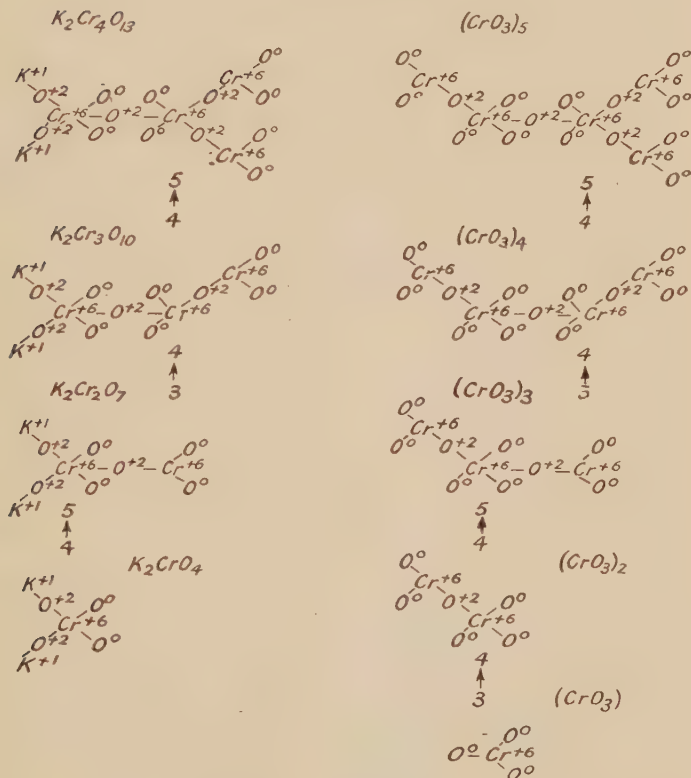
Subst.	Number of surplus electrons.	Experi- mental mol. sus.	Sum of ionic values.	Paramagnetism of one Cr^{+6} atom.		Diamagnetism of valency electrons required to give one Bohr magneton per Cr^{+6} atom.	
				Assuming no valency correction.	Assuming valency correction of 5 per pair of electrons.	Total for all valency electrons.	Per pair of valency electrons.
K_2CrO_4 ..	16	0.0	-56.36	56.36	96.36	571.64	71.66
$\text{K}_2\text{Cr}_2\text{O}_7$..	28	+54.0	-75.23	64.61	99.61	563.39	80.48
$\text{K}_2\text{Cr}_3\text{O}_{10}$..	40	+95.0	-94.1	63.0	96.4	565.0	84.75
$\text{K}_2\text{Cr}_4\text{O}_{13}$..	52	+193.0	-112.97	76.49	108.99	551.51	84.84
CrO_3	12	+41.0	-18.87	59.87	89.87	568.13	94.69
Na_2CrO_4 ..	16	+19.4	-31.36	50.76	90.76	577.24	72.15

We can, however, extend our speculations further with this second trial structure if we take the liberty of assuming still higher values for the valency diamagnetism. We may assume higher principal quantum numbers for the valency electrons, even if we are precluded from making similar assumptions for the subatomic electrons. As shown in Table II., in order to obtain the theoretical minimum paramagnetism of 628 we require for the chromates of potassium valency corrections per Cr^{+6} atom of values ranging from 551.51 to 571.64. This is equivalent to a diamagnetism of from 84.84 to 71.66 per pair of valency electrons. These very high values, which at first

appear very improbable. claim our serious consideration when we bear in mind that, other things being unchanged, it only requires raising the principal quantum number

Third Trial Structure.

TABLE III.



from 1 to 3 to increase the diamagnetism to 81 times the original value. Can it be then that we have in a very high value for valency diamagnetism the reason for the anomalously low values for paramagnetism referred to at the beginning of the paper?

We have adopted the above structures instead of a set both simpler and more alike for all the chromates. Our reason for doing so will be explained below.

In studying the paramagnetic susceptibilities of the above-mentioned four chromates of potassium it occurred to us to compare the experimental molecular susceptibilities of these with that of chromium trioxide, and to inquire to what extent additivity holds when chromium trioxide is added a molecule at a time to the lowest chromate, K_2CrO_4 , to obtain the three higher ones.

We carried out a similar inquiry regarding the molecular volumes of all these substances.

The results of these two investigations are shown in Table IV.

It must be understood that the numbers in Table IV. are all from experimental results, and that the chromium trioxide molecular paramagnetism used in the calculations is from the experimental figure obtained by us for solid chromium trioxide, which, however, probably is in a polymeric state. Accordingly the addition of this solid chromium trioxide, a molecule at a time, involves two reactions—first, the depolymerization of the chromium trioxide, which has a deparamagnetizing effect, and subsequently the addition of single molecules of chromium trioxide to single molecules of a chromate to give single molecules of another chromate of higher complexity, this rise in complexity having a paramagnetizing effect. It seems essential for a proper understanding of the magnetic properties of the chromates to consider these two magnetically opposing reactions—depolymerization and complex formation.

Therefore the first step in the rise in complexity should be written $xK_2CrO_4 + (CrO_3)x \rightarrow xK_2Cr_2O_7$, and similar equations should be assigned to the other two steps. It is clear that the departure from additivity will be an increase or a decrease according as the paramagnetizing effect of the complex formation is greater or less than the deparamagnetizing effect of the depolymerization.

It will be seen from Table III. that a step in the rise of complexity or rise in polymerization involves at one of the chromium atoms a change in the number of bonds either from 3 to 4 or from 4 to 5, the latter causing we suppose the greater increase in paramagnetism. When polymerized solid chromium trioxide is added, a molecule at a time, to give any one of the three different steps in complex formation the depolymerization must be the same, whichever step we are considering, even when the method of complex formation is different for the different steps.

TABLE IV.

Substance.	Molecular paramag. sus.		Molecular volume.	
	Experimental.	For additivity. Increase over additivity.	Experimental.	For additivity. Increase over additivity.
K_2CrO_4	0.0		71.12	
$K_2Cr_2O_7$	54.0	$K_2CrO_4 + CrO_3 = 41$	108.9	$K_2CrO_4 + CrO_3 = 107.09$ 1.81
$K_2Cr_3O_{10}$..	95.0	$K_2Cr_2O_7 + CrO_3 = 95$	148.8	$K_2Cr_2O_7 + CrO_3 = 144.87$ 3.93
$K_2Cr_4O_{13}$..	193.0	$K_2Cr_3O_{10} + CrO_3 = 136$	186.5	$K_2Cr_3O_{10} + CrO_3 = 184.77$ 1.73
CrO_3	41.0		35.97	

Thus any difference observed in the net result for the different stages must be due to difference in the structure of the complexes.

The increase in the number of bonds round a chromium atom causes a rise in paramagnetism because there is an increase in the total number of bonds and the extra bond is always paramagnetic. A rise is also caused because the increase in the number of bonds increases the interchange in the original bonds. There will also be a slight deparamagnetizing effect due to the charge-change in $0^\circ \rightarrow O^{+2}$, but this is masked by the greater paramagnetizing effect.

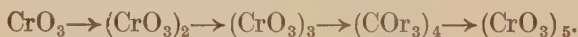
The results in Table IV. clearly show an alternation both in molecular paramagnetism and in molecular volume in the successive steps



This suggests a corresponding alternation in molecular structure such as we give in Table III. This implies an alternation in the mechanism of union at the successive additions of chromium trioxide, a molecule at a time.

In the first step, $K_2CrO_4 \rightarrow K_2Cr_2O_7$, 4 chromium bonds are increased to 5, or 8 chromium valency electrons become 10, which is the maximum number for the 3d layer (the outermost layer in Cr). Therefore, in the second step, $K_2Cr_2O_7 \rightarrow K_2Cr_3O_{10}$, the CrO_3 must be attached to another Cr atom, at which 3 bonds become 4, or 6 valency electrons become 8. At the third step, $K_2Cr_3O_{10} \rightarrow K_2Cr_4O_{13}$, these 8 can and do become 10.

In Table III. an analogous set of steps appears in the polymerization of chromium trioxide:



The second step in this progression corresponds to the first step in the chromate series.

The more the number of bonds attached to an atom the greater is the tendency to bond paramagnetism. Thus we expect a greater paramagnetic increase in the bond change $4 \rightarrow 5$ than in $3 \rightarrow 4$. Again, the change $4 \rightarrow 5$ upsets the compactness of the structure less than $3 \rightarrow 4$, and therefore the volume change is greater in $3 \rightarrow 4$ than in $4 \rightarrow 5$.

Table V. shows the magnetic relations of chromium trioxide and the chromates.

Starting from the experimental susceptibility obtained for solid chromium trioxide, we *assumed* for this solid various degrees of polymerization, and calculated what would be the average magnetism per bond for each assumed polymerization. From Table V, it appears that the greater the *assumed* degree of polymerization the smaller is the average magnetism per bond. On the other hand, if we started with solid chromium trioxide, and by some experimental treatment increased the degree of polymerization,

TABLE V.

	Experi- mental mol. sus.	Sum of ionic diamag- netisms.	Number of bonds.	Magnet- ism of bonds.	Average magnet- ism per bond.	Percentage proportion of chrom- ium-oxygen bonds in each molecule.
(CrO ₃) ₆	+246.0	-153.52	23	+399.52	+17.37	100
(CrO ₃) ₅	+205.0	-128.45	19	+333.45	+17.55	
(CrO ₃) ₄	+164.0	-103.38	15	+267.38	+17.82	
(CrO ₃) ₃	+123.0	-78.31	11	+201.31	+18.30	
(CrO ₃) ₂	+82.0	-53.24	7	+135.24	+19.32	
CrO ₃	+41.0	-28.17	3	+69.17	+23.06	
K ₂ Cr ₄ O ₁₃ . .	+193.0	-137.77	18	+330.77	+18.37	88.8
K ₂ Cr ₃ O ₁₀ . .	+95.0	-112.70	14	+207.7	+14.83	85.7
K ₂ Cr ₂ O ₇ . .	+54.0	-87.63	10	+141.63	+14.16	80.0
K ₂ CrO ₄ . .	0.0	-62.56	6	+62.56	+10.43	66.6
Na ₂ CrO ₄ . .	+19.4	-37.56	6	+56.96	+9.49	66.6

then the average magnetism per bond would become *greater*.

The average magnetism per bond, as shown in Table V, for the chromates of potassium, increases with rise in complexity, and was calculated by including the potassium-oxygen bonds. By omitting these bonds the average for chromium-oxygen bonds would appear somewhat larger than that given in Table V.

All the average bond magnetisms as given in Table V, for the chromates of potassium, except that for the

tetrachromate, are below the average for any of the given polymers of chromium trioxide. However, the uncertainty, as determined for the tetrachromate measurements, is so large that the true average in this case also might be below the chromium trioxide values.

If we assume, from colour differences for example, that the average in the trioxide should be greater than the greatest in the chromates, then there is an upper limit to the degree of polymerization. This might be put at $(\text{CrO}_3)_5$. There is also a lower limit, since we must have at least the polymer $(\text{CrO}_3)_3$ for the purpose of the present theory, $(\text{CrO}_3)_2$ being of no use. There seems, then, to be a choice between $(\text{CrO}_3)_5$, $(\text{CrO}_3)_4$ and $(\text{CrO}_3)_3$. The two lower polymers satisfy best the requirement that the average paramagnetism per bond be greater than the average in the chromates. However, this requirement does not definitely exclude $(\text{CrO}_3)_5$, especially when we bear in mind the uncertainty in the measurements for the tetrachromate. Further, when we consider what relation is necessary between the paramagnetic effect of the step 4 bonds \rightarrow 5 bonds and that of the step 3 \rightarrow 4, we find that $(\text{CrO}_3)_5$ requires only that $(4 \rightarrow 5)$ be $> 1\frac{1}{2}$ ($3 \rightarrow 4$), whereas $(\text{CrO}_3)_4$ and $(\text{CrO}_3)_3$ both require that $(4 \rightarrow 5)$ be > 2 ($3 \rightarrow 4$). On the whole, then, there is an advantage in adopting $(\text{CrO}_3)_5$, for which the magnetic relations are as shown in Table VI.

Whatever polymer we adopt for chromium trioxide, its bonds have a large paramagnetism. This very marked homopolar character is retained in the internal bonds of the complex anion of the chromates, although the paramagnetism of each bond does not remain unchanged when the chromate is formed. The bonds outside the complex anion (the alkali-oxygen bonds), which are heteropolar, may be regarded as diamagnetic. When the proportion of these alkali-oxygen bonds in the molecule is large, as in the monochromates, then their counteracting influence is great and the average paramagnetism per bond is small compared with that in the trioxide. The larger the proportion of chromium-oxygen bonds in the molecule the nearer does the average paramagnetism per bond come to that in the trioxide.

In the sequence of steps

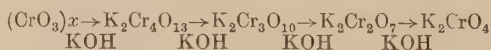


TABLE VI.
Rise in Paramagnetism above Additivity.

	Total rise.	Rise in cores.	Rise in bonds.	Paramagnetic effect owing to change in number of bonds. in complex formation, depolymerization.
$5\text{K}_2\text{CrO}_4 + (\text{CrO}_3)_5 \rightarrow 5\text{K}_2\text{Cr}_2\text{O}_7$	5×13	3.1	61.9	$5(4 \rightarrow 5) > 2(5 \rightarrow 4) + 2(4 \rightarrow 3)$ or $3(4 \rightarrow 5) > 2(4 \rightarrow 3)$
$5\text{K}_2\text{Cr}_2\text{O}_7 + (\text{CrO}_3)_3 \rightarrow 5\text{K}_2\text{Cr}_3\text{O}_{10}$	0	3.1	—3.1	$5(3 \rightarrow 4) < 2(5 \rightarrow 4) + 2(4 \rightarrow 3)$ or $3(3 \rightarrow 4) < 2(5 \rightarrow 4)$
$5\text{K}_2\text{Cr}_3\text{O}_{10} + (\text{CrO}_3)_5 \rightarrow 5\text{K}_2\text{Cr}_4\text{O}_{13}$	5×57	3.1	281.9	$5(4 \rightarrow 5) > 2(5 \rightarrow 4) + 2(4 \rightarrow 3)$ or $3(4 \rightarrow 5) > 2(4 \rightarrow 3)$

there is a progressive loss of paramagnetism in the chromium-oxygen bonds (though the progression fluctuates), or a progressively less free interchange of the valency electrons between the Cr and the O atoms, with a corresponding increase in the stability of the submolecular structure.

Associated with a progression of this nature we very often see a colour change in the direction black \rightarrow red \rightarrow yellow . . . \rightarrow white, the looser structure corresponding with greater absorption of visible light. Thus we see in the present instance the change from the dark red of chromium trioxide, through the slightly less dark red of the tetrachromate, and the brighter reds of the trichromate and dichromate, to the bright yellow of K_2CrO_4 . Similarly, we have HgS red or black, CdS yellow, ZnS white; HgO red, CdO brown, ZnO white.

Associated with this correlation of stability and colour we have the loosening action of heat when it causes a change in colour along the spectrum towards the red end, *e. g.* :—

ZnO white (cold), yellow (hot).

PbO light buff (cold), brown-red (hot).

This action of heat suggests the question of the effect of temperature upon the anomalous paramagnetism of the chromates. Raising the temperature should *raise* this kind of paramagnetism, instead of producing a *lowering* effect, as in the case of normal paramagnetism. It is true that Weiss and Collet found $K_2Cr_2O_7$ solution to have a susceptibility constant to within 2 per cent. between 14° and 50° ; but it is quite possible, with more refined methods or at higher temperatures, that evidence will be forthcoming in support of our conclusion. Indeed, several instances are already known among the elements (Cr itself for example) where increase of paramagnetism has been observed when the temperature is raised. To clear up this point further research would be of great value.

The action of potassium hydroxide upon chromium trioxide has an analogue in the action of water, which produces a series of similar complexes, thus causing a reduction of paramagnetism. Accordingly, we find that the paramagnetic susceptibility of chromium trioxide obtained from measurements on aqueous solutions is less than that obtained from the solid substance.

Mol. sus. (from solid) = $+40.6 \pm 1.1$.

(from aqueous solutions) average = $+38.85$.

It is impossible to find the degree of polymerization of chromium trioxide by a determination of the molecular weight in aqueous solutions, because, as just mentioned, water immediately breaks up any polymer of chromium trioxide into a mixture of chromic acids of different degrees of complexity, the percentage of each depending upon the concentration of the solution.

A contrast of the results for the chromate of sodium and for that of potassium yields an interesting result. The diamagnetism of the two sodium-oxygen bonds in Na_2CrO_4 is greater than that of the two potassium-oxygen bonds in K_2CrO_4 by 5.6 or 2.8 per bond. Similarly, the bond in NaCl is more heteropolar (more diamagnetic) than that in KCl .

Experimental.

The magnetic measurements were made with an improved form of Curie-Chénevau magnetic balance as described in "The Diamagnetism of Polyhalides," by Gray and Dakers *, except that the torsion wire was of platinum and the temperature arrangements were different.

The temperature inside the balance case was noted before and after each measurement. Although the temperature was not constant, sudden changes and differences in different parts of the apparatus were avoided by having the whole balance in a small enclosure. Further, the temperature did not vary very much, and any variation did not seem to affect the susceptibility in any pronounced way.

The solids were measured in as finely divided a form as possible, and in reducing the materials to a powder special precautions had to be taken to prevent absorption of moisture, especially in the case of the trichromate, tetrachromate, and chromium trioxide. Chromium trioxide had to be handled very quickly in transferring to the container, on account of its very deliquescent nature.

In addition, the magnetic susceptibility of chromium trioxide was determined from measurements with aqueous solutions at several different concentrations.

Chromium trioxide.—A quantity of specially pure chromium trioxide was obtained from British Drug Houses, and

* Phil. Mag. xi, p. 81.

a quantity was also prepared according to the directions given by Zettnow in *Pogg. Annal.* cxliii. pp. 468-473 (1871).

Analysis was carried out by the ammonium ferrous sulphate method. As shown below, both the B.D.H. specimen and our own preparation were found to be very pure. Two procedures were adopted in the analysis: in one, excess of ammonium ferrous sulphate was titrated against standard potassium dichromate, in the other, an aqueous solution of chromium trioxide was

TABLE VII.

Analyses.

Compound.	Preparation.	Number of Analyses.	Percentage purity.
CrO ₃	B.D.H.	3	99.96
	Prep.	2	100.1
K ₂ CrO ₄	B.D.H.	2	100.09
K ₂ Cr ₂ O ₇	B.D.H.	—	Standard.
K ₂ Cr ₃ O ₁₀	Prep. 1	3	99.995
	„ 2	3	99.63
K ₂ Cr ₄ O ₁₃	Prep. 1	3	98.8
	„ 2	2	97.2
	„ 3	1	97.4
	„ 4	2	98.96
	„ 5	1	99.13

used to titrate against known weights of ammonium ferrous sulphate (see Table VII.). Four magnetic measurements were carried out with the solid, three with the B.D.H. specimen, and one with our own preparation (see Table IX.).

In the case of the aqueous solutions two series of measurements were carried out:—

(1) A series of 12 measurements on solutions with compositions varying from 3.962 mols of water per mol of CrO₃ to 18.89 mols of water per mol of CrO₃.

(2) A series of 9 measurements on solutions with compositions varying from 3.927 mols of water per mol of CrO₃ to 16.71 mols of water per mol of CrO₃ (see Table III.).

Potassium chromate.—Specially pure material from British Drug Houses was used. It was analysed by the ammonium ferrous sulphate method, as in the case of chromium trioxide (see Table VII.). It was very difficult to obtain magnetic measurements of high precision, on account of the very low susceptibility. Sometimes it appeared to be slightly paramagnetic, sometimes slightly diamagnetic. Altogether 21 measurements were made on 15 different samples of potassium chromate. The mean value was taken (see Table IX.).

Potassium dichromate.—The specially pure material supplied by British Drug Houses for analytical purposes was used. It was assumed to be 100 per cent. pure, and taken as a standard for analysis (see Table IX. for mol. sus.).

TABLE VIII.

Chromium Trioxide in Aqueous Solutions.

Range of concentrations.	Temp. range.	Number of solutions.	Average spec. sus. of CrO_3 .
1 mol CrO_3 : 3.962 mols H_2O } to	12.8° to	12	+0.387
1 mol CrO_3 : 18.89 mols H_2O }	14.2° C.		
1 mol CrO_3 : 3.927 mols H_2O } to	12.5° to	9	+0.39
1 mol CrO_3 : 16.71 mols H_2O }	13.7° C.		

Potassium trichromate.—This compound was prepared by the method given in Roscoe and Schorlemmer's 'Chemistry,' ii. p. 1064. To 50 c.c. of nitric acid (sp. gr. 1.19 approx.) a quantity of potassium dichromate was added, and the whole heated to boiling-point, when the dichromate dissolved. Crystals of potassium nitrate separated on cooling. These were removed, and a further quantity of the dichromate was added to the solution. This was heated and cooled as before, the potassium nitrate being again separated. This process was repeated till a quantity of red crystals of the trichromate were obtained on cooling. These crystals were very pure and fairly large. They were drained on a porous plate, and then dried by heating at about 100° C. on a sand bath. Two quantities were

prepared in this way. Both preparations were analysed after magnetic measurements had been made. The method of analysis was as for the monochromate (see Table VII.). Five different samples were measured magnetically—two from the first preparation, and three from the second.

Potassium tetrachromate.—This compound was prepared by the method given in Roscoe and Schorlemmer's 'Chemistry,' ii. p. 1065. To 20 c.c. of nitric acid (sp. gr. 1.4 approx.) was added 10 grams of potassium dichromate. The dichromate was brought into solution by heating to 70° C. On cooling slowly crystals of the tetrachromate separated. These were removed by decantation and drained on a porous plate. They were then washed with a small quantity of nitric acid and again drained for a short time.

TABLE IX.

Compound.	Temp. range.	Number of measurements.	Mol. sus.	Percentage error.
CrO_3	12.7° to 15.5°	4	+ 41.0 ± 1.1	2.7
K_2CrO_4 ..	12.8° to 18°	21	0.0	
$\text{K}_2\text{Cr}_2\text{O}_7$..	13.6° to 17.6°	7	+ 54.0 ± 1.4	2.6
$\text{K}_2\text{Cr}_3\text{O}_{10}$..	14.3° to 15.1°	5	+ 95.0 ± 2.9	3.0
$\text{K}_2\text{Cr}_4\text{O}_{13}$..	13.6° to 18.3°	15	+193.0 ± 11.9	6.2

Finally, they were dried by heating on a sand bath to 110° C.

There was some difficulty in obtaining pure potassium tetrachromate in this preparation. Chromium trioxide tended to be formed at the same time. In all, five different quantities of the compound were prepared. The substance was analysed by the method described for the monochromate (see Table VI.).

Fifteen magnetic measurements were made on twelve samples taken from the five preparations. Six of the samples were taken from the product of the last preparation, which the analysis indicated to be the purest of the five (see Table IX.).

Mr. John Dakers desires to thank The Department of Scientific and Industrial Research for allowance during one year of the period occupied in this research.

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XXIII. *On the Radiation Emitted by Compressed Crystalline Substances under High Potentials.* By ISAY A. BALINKIN, B.S.M.E., M.S., Ph.D., University of Cincinnati*.

[Plates V. & VI.]

I. *Introduction.*

IN a period of years (1922-1925) M. G. Reboul published three articles dealing with a new method of producing a very absorbable radiation when a heterogenous material of high electrical resistance is subjected to a potential difference of 100 to 10,000 volts. In the last article⁽¹⁾ the radiating source is made of compressed powder of different crystalline substances. The emission from such a "radiating cell" was found by Reboul to affect the photographic plate and also to produce ionization. By measuring the absorption coefficient of air and very thin films of celluloid the range of radiation was placed between the soft X-rays and short ultra-violet.

The experiments described in this paper were undertaken with the object of reproducing the results obtained by Reboul. The findings confirmed the possibility of constructing a radiating cell whose emission is entirely of an absorbable nature. It was found, however, that a number of factors which were not mentioned by Reboul required a careful control; therefore, the construction of such a radiating cell is given in detail.

The second part of the paper deals with a test that reveals the mechanism of such radiation proving that it is emitted not by the cell *per se*, but that it finds its origin in the gases escaping from the bottom of the cell.

II. *The Radiating Cell and its Accessories.*

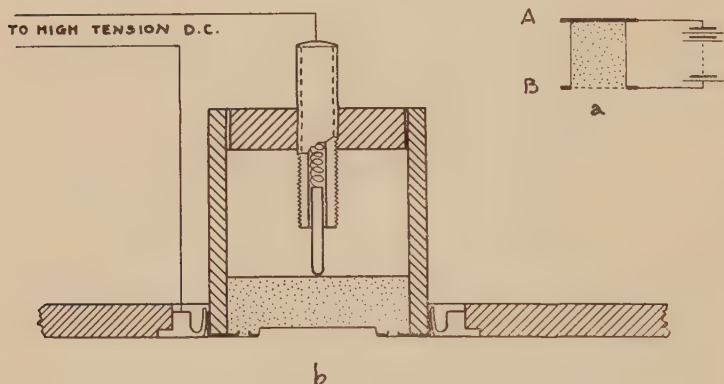
The description of the radiating cell used by Reboul is limited to a few lines:—"La cellule à rayonnement comprend, en principe, une pastille d'un sel qui a été d'abord finement pulvérisé, puis aggloméré à la presse à pastiller." If such a block of compressed crystalline powder be placed between two electrodes A and B (fig. 1, *a*), the lower of which is a metallic gauze, upon the application of potential a large number of minute sparks can be observed at places

* Communicated by the Author.

where the gauze does not make a good contact with the compressed powder. It was imperative, therefore, to construct a radiating cell in such a manner as to eliminate any arcing at the junction of the lower electrode and the crystalline powder.

The final form of the radiating cell, which in every way proved to be satisfactory, is represented in fig. 1, *b*. An outer shell was found to be essential, due to the fact that under low pressures the cohesion between the grains of the powder was not sufficient to bind the whole mass into one solid block. A fibre tube, 1.6 cm. inside diameter and 2.0 cm. high, was used for this purpose. Since this tube would not withstand pressures above 50 kg./cm.², it was

Fig. 1.



The radiating cell.

necessary to insert it into a strong steel ring during compression. A lower terminal was made of a sheet of tin foil .01 mm. thick. The central part of the foil had a hole 1.1 cm. diameter with twelve small holes punched around it. Some powder was compressed into these small holes, and thus united firmly the crystalline substance with the lower terminal. The upper terminal consisted of a circular disk of bakelite which accurately fitted into the fibre tube. Through the centre of this disk passed a screw with a little plunger. The latter was pushed against the compressed powder by a small helical spring located inside the screw.

The making of the cell consisted of the following operations. The material to be investigated was powdered in a mortar, then passed through a silk sieve, and retained on another sieve of a finer mesh. In this manner it was possible to secure grains of a definite uniformity ranging between the upper and the lower limits of the two sieves employed. The amount of powder used in all the experiments was 1 gram. The fibre tube was forced into the steel ring and the lower terminal attached by putting some glue on the lower edge of the tube. The ring with the tube and the terminal was then placed on a steel base, the central part of which was elevated, so that after compression it left an indentation in the middle portion of the bottom, as shown in fig. 1, *b*. The powder was then put into the tube, and a steel plunger forced down until the required pressure was obtained.

After compression the fibre tube was forced out of the ring. The tin foil terminal was bent around the edge of the fibre tube to provide contacts when the latter was inserted into a brass ring in the cell holder. The upper terminal was then attached to the tube, and in this form the cell was ready to be placed in a light-tight box for the investigation of its characteristic radiation. The radiation from the cell was recorded on a commercial grade of a photographic film located directly under the bottom of the emitting surface.

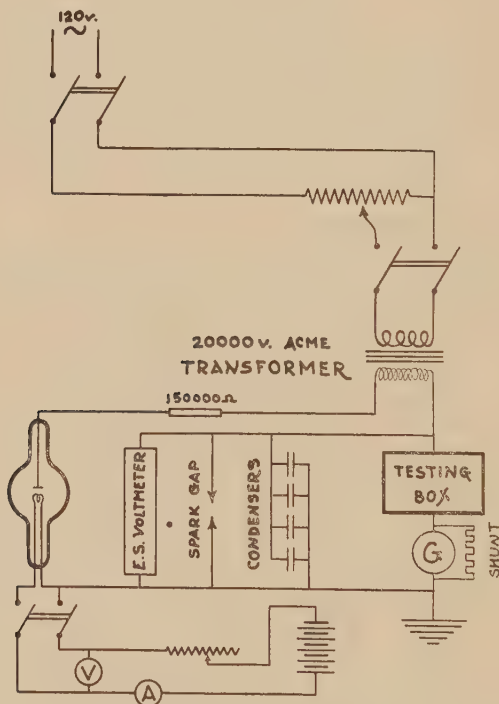
As stated before, the character of the radiation depends upon a number of factors. In order to be able to investigate the influence of every one of these factors, six radiating cells were usually constructed under identical conditions, with the exception of one factor, which was assumed to affect the nature of the radiation. This one factor was made to vary in steps from one cell to another, and then, from the effect produced on the photographic film, it was possible to establish the importance of that factor in influencing the character of the radiation.

The general view of the light-tight box, with the six radiating cells and the film holders in place, is given on fig. 2 (Pl. V.). The box was constructed of bakelite, lined with black velvet in order to eliminate the possibility of any spurious effects due to the reflexions from the walls.

The film, half-covered with a sheet of celluloid or cellophane as an absorber, was fastened to a brass plate mounted on a tube passing through the double walls of the box.

The upper terminals of the radiating cells were connected to the negative side of the high tension, while the bottom terminals were at the ground potential. In order to prevent any electrical discharge between the bottom of the cells and the film holders the latter were also connected to the ground.

Fig. 3.



The diagram of connexions.

III. *Experimental Arrangements.*

The diagram of connexions on fig. 3 represents the arrangement of the apparatus employed in this research. A 120-volt A.C. line was connected across an auto-transformer which fed the primary of a 20,000 volt Acme transformer. The secondary of the transformer was connected through a 150,000 ohms protecting resistance to a Kenotron rectifying tube and to the testing box containing the radiating cells. Because of only half-wave rectification

several condensers, each of .0017 M.F. capacity, were connected in parallel in order to smooth out the rectified waveform.

A galvanometer was placed on the ground side of the circuit and could measure the current passing through any one of the six radiating cells. A variable shunt resistance was connected across the galvanometer, so that its sensitivity could be varied from 2×10^{-8} to 3×10^{-6} ampere per division.

An electrostatic voltmeter with a range from 500 to 10,000 volts was used to measure the e.m.f. applied to the radiating cells.

IV. *Results.*

All radiating cells used in this investigation were made of compressed powder of alum, $\text{Al}_2(\text{SO}_4)_3 \cdot \text{K}_2\text{SO}_4 \cdot 24\text{H}_2\text{O}$, although NaCl and other crystalline substances gave similar results. The effects produced by the radiating cells on the photographic film are shown in fig. 4 (Pl. VI.). The variable factor in these cells was the size of the crystalline grains, which ranged as follows:—(a) .0296 in., (b) .0125 in., (c) .0080 in., (d) .0057 in., (e) .0032 in., and (f) .0025 in. The other constant factors were:—pressure 275 kg./cm.², potential 5000 volts, humidity 52 per cent. The film was placed at a distance of 3 mm. from the bottom of the radiating cells, the current through the cells was about the same, being equal to 10^{-6} amp., and the time of exposure thirteen hours.

The first four prints (a, b, c, d) indicate the presence of visible radiation. This is concluded from the fact that the intensity on the lower part of the film is practically the same as on the upper part, which was covered with a sheet of celluloid .13 mm. thick. If there were any absorbable radiation present, there would be a difference in the intensity such as is noticeable in the last two prints c and d.

A very similar set of prints was obtained when the pressure was the variable factor:—(a) 2250 kg./cm.², (b) 1360 kg./cm.², (c) 680 kg./cm.², (d) 350 kg./cm.², (e) 110 kg./cm.², (f) 25 kg./cm.². The other constant factors were: size of the grains .0025 in., potential 5000 volts, humidity 54 per cent.

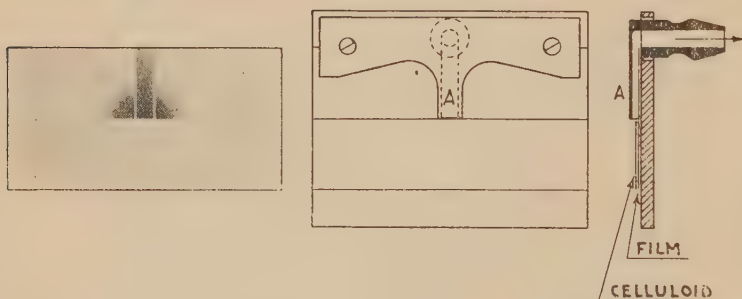
After a large number of experiments the following factors were found to control the character of the emission from the radiating cells: (1) applied potential, (2) relative humidity

of the air, (3) size of the crystalline grains, and (4) pressure used in compressing the powder.

The necessary conditions under which an alum radiating cell emits only absorbable radiation can be stated as follows:—For an applied potential of 5000 volts the powder must be prepared and compressed in an atmosphere of relative humidity of not more than 55 per cent., the average size of the grains being less than $\cdot 0032$ in., and the force of compression below 300 kg./cm.^2 .

Under the above conditions the emission from the radiating cell is completely absorbed by celluloid $0\cdot 13 \text{ mm.}$ thick and only partially absorbed by celophane $\cdot 02 \text{ mm.}$ thick. This indicates that the range of the radiation lies between the extreme ultra-violet and soft X-rays.

Fig. 5.



V. The Mechanism of the Emission.

According to the explanation offered by Reboul, the emission of very absorbable radiation from compressed crystalline substance takes place from the bottom layer of the radiating cell. A potential drop from several volts up to several hundred volts may exist at the discontinuities, and when electrons traverse that gap they collide with the molecules of the crystalline substance. The wave-length of the emitted radiation is given then by the quantum relation

$$\lambda = \frac{hc}{Ve}.$$

It was the purpose of the following experiment to determine whether the radiation is emitted by the bottom layer of the cell itself or the gas that may be escaping from that bottom. The arrangement employed is shown on fig. 5.

It consisted of a semicircular tube A through which air could be drawn from the close proximity of the bottom of the cell and passed over the photographic film. The lower part of the film was covered with thin celluloid, to be certain whether only absorbable radiation was present. The reproduction of the film shown on the same figure indicates that darkening was produced also under the semicircular tube. This darkening, gradually decreasing in intensity, extends along the path of the incoming air. If the radiation were emitted by the bottom of the cell *per se*, the film would show no darkening under the semicircular tube. The contrary result is a conclusive evidence that the air escaping from the bottom of the cell is the source of very absorbable radiation.

To explain this we have to consider first the mechanism of conduction through such a non-homogeneous substance as compressed crystalline powder of alum. Its total resistance is made up of an arrangement of resistances and capacities in series and in parallel, so that when a sufficiently high potential is built a spark discharge will occur at the place of discontinuity. The air in the interstices of the powder will become ionized, and if the material is sufficiently porous there will be a transfer of ions in the electrostatic field maintained by the applied potential. When the ionized or excited molecules of the air escape from the pores of the compressed powder they either recombine or return to their normal states with the corresponding emission of radiation.

Assuming this to be a true picture of the mechanism of radiation from compressed crystalline substances, we can form a definite idea as to the lower limit of the wavelengths. These are the K lines of oxygen, 23.7 A.U., and nitrogen, 31.7 A.U.

The radiation from the air of very absorbable nature was originally discovered by E. Wiedemann⁽²⁾ in a spark discharge at atmospheric pressure. Not knowing the nature of such radiation, Wiedemann attributed its thermo-luminescent effect to "Entladungsstrahlen." These effects were more fully investigated by M. H. Hoffmann⁽³⁾. Shortly afterwards J. J. Thomson⁽⁴⁾ observed the ionization produced by the "Entladungsstrahlen," and, using this method, E. Laird⁽⁵⁾ determined the absorption coefficients for different gases and very thin films of collodion, mica, and other substances. Her conclusion was that "Entladungs-

strahlen " are of electromagnetic nature and belong to the wave-length range shorter than ultra-violet.

Recently in a number of papers J. J. Thomson ⁽⁶⁾, M. A. Dauvillier ⁽⁷⁾, and Halweck ⁽⁸⁾ investigated the radiation emitted during a discharge through gases at reduced pressures. Their conclusions are that during a discharge the emission consists of the characteristic line spectra of the gases superimposed on a continuous background of soft X-rays region.

Thus the "Entladungsstrahlen," the discharge of electricity through gases at reduced pressures, and the new source of soft X-rays from compressed crystalline substances belong essentially to the same class.

In conclusion, the author wishes to express his deep gratitude to Dr. L. T. More and Dr. R. C. Gowdy, whose kind interest and assistance made this research possible.

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XXIV. The Axially Symmetric Stationary Gravitational Field. By EDWARD S. AKELEY*.

CONTENTS.

1. The quadratic differential form.
2. Theorem I.—concerning the reduction of the equations in the case of non-isometric coordinates.
3. Theorem II.—concerning the reduction of the equations in the case of isometric coordinates.
4. A generalization of the Weyl-Levi-Civita theory of the axially symmetric static gravitational field.
5. The application of two types of power series expansions to the solution of the equations.
6. The application of the above types of expansion to the generalization of the Weyl-Levi-Civita theory.
7. The application of a power series expansion to the determination of the general solution of the equations in empty space.

* Communicated by the Author.

1. **W**E shall consider the Einstein field equations for an Einstein-Riemann space defined in the following manner:—There exists a coordinate system (x_0, x_1, u, v) where the coordinates have continuous ranges such that the metric differential form when expressed in terms of these coordinates is invariant under the following transformations:—

$$\begin{aligned} (a) \quad x_0 &= y_0 + \alpha, & \text{where } \alpha \text{ is any constant.} \\ (b) \quad x_1 &= y_1 + \beta, & \text{,, } \beta \text{ ,, ,,} \\ (c) \quad x_0 &= -y_0, \\ & x_1 = -y_1. & \text{. (1)} \end{aligned}$$

These conditions require that the line element of the field be of the form

$$A dx_0^2 + 2C dx_0 dx_1 + B dx_1^2 + F du^2 + 2K dudv + H dv^2,$$

where the coefficients are functions of u and v only. This form, however, can be reduced to either of the two types:

$$A dx_0^2 + 2C dx_0 dx_1 + B dx_1^2 + F du^2 + H dv^2, \quad (2.1)$$

$$A dx_0^2 + 2C dx_0 dx_1 + B dx_1^2 + J (du^2 + dv^2), \quad (2.2)$$

which forms will be considered exclusively in this paper. While in many ways the isometric form (2.2) may be better suited to a purely mathematical treatment, it is by no means obvious that it is the best one to use in the actual determination of gravitational fields. Other types of canonicalization may often be found more suitable, either because of their physical significance or because of singularities that may be introduced by insistence upon an isometric form. We shall further postulate that A , $-B$, $C^2 - AB$, $-F$, $-H$, $-J$ are all positive or zero in the region considered.

One instance of a physical situation where this type of form naturally suggests itself is found in the study of an axially symmetric distribution of matter rotating with uniform angular velocity about its axis of symmetry; although the possibility of gravitational radiation suggests that, if taken rigorously, the condition (c) may be unduly restrictive. In this particular case x_0 would correspond to the time coordinate, x_1 to the longitude angle, and u and v to coordinates in the meridian plane.

Once for all we shall fix certain matters of notation. Subscripts u and v will denote the differentiation with respect to u and v respectively. When using tensor notation (x_2, x_3) will replace (u, v) . If we have two functions

$$\phi(A, B, C, F, H)$$

then we shall define

$$\begin{aligned}\Delta^2\phi &= \phi_{uu}(A, B, C, F, H) + \frac{F}{H} \phi_{vv}(A, B, C, H, F), \\ [\phi, \psi] &= \phi_u(A, B, C, F, H) \psi_u(A, B, C, F, H) \\ &\quad + \frac{F}{H} \phi_v(A, B, C, H, F) \phi_v(A, B, C, H, F).\end{aligned}$$

This notation introduces an apparent dissymmetry in the equations which could be avoided by slight change of definition. However, the unsymmetrical form appears to have advantages in the actual determination of gravitational fields. It is to be noted that these definitions reduce to those given by Weyl* when $F = H$.

We shall introduce the transformation

$$\left. \begin{aligned} A &= e^{d+s} \cos \psi, \\ B &= -e^{d-s} \cos \psi, \\ C &= e^d \sin \psi, \\ F &= -e^{2f}, \\ H &= -e^{2h}, \\ J &= -e^{2j}, \end{aligned} \right\} \quad D = e^{2d}. \quad (4)$$

The components of the contracted Riemann-Christoffel tensor are given by

$$2FG_{00} = \Delta^2 A + 1/2D \{ B[A, A] - A[B, B] + 2A[C, C] - [A, C^2] \} + [A, h-f], \quad (5.1)$$

$$2FG_{11} = \Delta^2 B + 1/2D \{ A[B, B] - B[A, A] + 2B[C, C] - [B, C^2] \} + [B, h-f], \quad (5.2)$$

$$2FG_{01} = \Delta^2 C + 1/2D \{ [AB, C] - 2C[A, B] \} + [C, h-f], \quad (5.3)$$

$$\begin{aligned} G_{22} &= d_{uu} + du^2 - f_u du + 1/2H \{ F_v dv + H_{uu} + F_{vv} \\ &\quad - F_v(f_v + h_v) - H_u(f_u + h_u) \} \\ &\quad + 1/2D \{ A_u B_u - C_u^2 \}, \end{aligned} \quad (5.4)$$

$$\begin{aligned} G_{33} &= d_{vv} + dv^2 - h_v dv + 1/2F \{ H_u du + H_{vv} + F_{vv} \\ &\quad - H_u(f_u + h_u) - F_v(f_v + h_v) \} \\ &\quad + 1/2D \{ A_v B_v - C_v^2 \}, \end{aligned} \quad (5.5)$$

$$\begin{aligned} G_{23} &= d_{uv} + du dv - (h_u dv + f_v du) \\ &\quad + 1/4D \{ A_u B_v + A_v B_u - 2C_u C_v \}. \end{aligned} \quad (5.6)$$

* Weyl, *Ann. der Phys.* liv. p. 135 (1917).

It is readily shown that the equations

$$G_{ij} = -[T_{ij} - \frac{1}{2}g_{ij}(T + 2\lambda)], \quad . \quad . \quad . \quad (6)$$

for the form (2.1), where λ is a constant, are equivalent to the system :

$$\Delta^2 \psi - [s, s] \sin \psi \cos \psi + [\psi, d - f + h] = \Psi, \quad . \quad . \quad (7.1)$$

$$\Delta^2 s - 2[s, \psi] \tan \psi + [s, d - f + h] = S, \quad . \quad . \quad (7.2)$$

$$\Delta^2 d + [d, d - f + h] = D, \quad . \quad . \quad . \quad . \quad . \quad (7.3)$$

$$\Delta^2 h - \frac{1}{4}\{[d, d] + [\psi, \psi] - [s, s] \cos^2 \psi\} \\ + [h, h - f] = V, \quad . \quad . \quad (7.4)$$

$$d_{uu} - d_{vv} + \frac{1}{2}(d_u^2 - d_v^2 e^{2(f-h)}) \\ - \{d_u(f_u + h_u) - d_v(f_v + h_v) e^{2(f-h)}\} \\ - \frac{1}{2}\{\psi_u^2 - \psi_v^2 e^{2(f-h)}\} \\ + \frac{1}{2}\{s_u^2 - s_v^2 e^{2(f-h)}\} \cos^2 \psi = 2W, \quad (7.5)$$

$$d_{uv} + \frac{1}{2}d_u d_v - (h_u d_v + f_v d_u) \\ - \frac{1}{2}(\psi_u \psi_v - s_u s_v \cos^2 \psi) = U, \quad . \quad (7.6)$$

where the right-hand members are defined by

$$\Psi = E \cot \psi - \frac{e^{2f-d}}{\sin \psi} \{[T_{00} - \frac{1}{2}g_{00}(T + 2\lambda)] \\ e^{-s} - [T_{11} - \frac{1}{2}g_{11}(T + 2\lambda)] e^{+s}\}, \quad . \quad . \quad . \quad (8.1)$$

$$S = \frac{e^{2f-d}}{\cos \psi} \{[T_{00} - \frac{1}{2}g_{00}(T + 2\lambda)] e^{-s} \\ + [T_{11} - \frac{1}{2}g_{11}(T + 2\lambda)] e^{+s}\}, \quad . \quad . \quad . \quad (8.2)$$

$$E = e^{2f-d} \{2C[T_{01} - \frac{1}{2}g_{01}(T + 2\lambda)] - B[T_{00} - \frac{1}{2}g_{00}(T + 2\lambda)] \\ - A[T_{11} - \frac{1}{2}g_{11}(T + 2\lambda)]\}, \quad . \quad . \quad . \quad . \quad (8.3)$$

$$V = -\frac{1}{2}\{[T_{22} - \frac{1}{2}g_{22}(T + 2\lambda)] \\ + [T_{33} - \frac{1}{2}g_{33}(T + 2\lambda)] e^{2(f-h)}\} - \frac{1}{2}E, \quad . \quad (8.4)$$

$$W = -\frac{1}{2}\{[T_{22} - \frac{1}{2}g_{22}(T + 2\lambda)] - [T_{33} - \frac{1}{2}g_{33}(T + 2\lambda)] e^{2(f-h)}\}, \\ . \quad . \quad . \quad (8.5)$$

$$U = -[T_{23} - \frac{1}{2}g_{23}(T + 2\lambda)]. \quad . \quad . \quad . \quad . \quad . \quad (8.6)$$

Now, if we consider the $T^{\mu\nu}$ as given functions of (u, v) the identical vanishing of the $\text{div} [G_j^i - g_j^i(G - 2\lambda)]$ require that the g_{ij} satisfy the equation

$$(T^i_i)_i = 0,$$

and we obtain the following two first-order differential equations to be added to the set (7) :

$$\frac{1}{2}\Psi\psi_u - \frac{1}{2}Ss_u \cos^2 \psi - \frac{1}{2}(Ee^{-2f})ue^{2f} + Vd_u \\ + (We^{d+2(h-f)})ue^{-d+2(f-h)} + (Ue^{d+f-h})ve^{-d} = 0, \quad (10.1)$$

$$\frac{1}{2}\Psi\psi_v - \frac{1}{2}Ss_v \cos^2 \psi - \frac{1}{2}(Ee^{-2f})ve^{2f} + Vd_v \\ - (We^d)ve^{-d} + (Ue^{d+h-f})ue^{2(f-h)-d} = 0. \quad (10.2)$$

2. We state the following:—*Theorem I.*—A set of functions (ψ, d, s, f, h) which satisfy equations (10) as well as (7.3), (7.5), and (7.6), and which also satisfy one of the equations (7.1), (7.2) or (7.3), also satisfy the remaining two equations of this group if the corresponding determinant

$$\begin{vmatrix} \psi_u & \psi_v \\ s_u & s_v \end{vmatrix} \cos^2 \psi, \quad \begin{vmatrix} \psi_u & \dot{\psi}_v \\ d_u & d_v \end{vmatrix} \quad \text{or} \quad \begin{vmatrix} s_u & s_v \\ d_u & d_v \end{vmatrix} \cos^2 \psi,$$

is not zero.

In order to prove this, we replace (Ψ, S, E, W, U, V) in (10) by the corresponding right-hand members of (7), obtaining two identities. If now we subtract these identities from the corresponding equations (10) which we assume to be satisfied, and if we assume (7.3), (7.5), and (7.6) are satisfied, we obtain the two equations

$$\frac{1}{2}\psi_u \{ \Psi - [\Delta^2 \psi - [s, s] \sin \psi \cos \psi + [\psi, d - f + h]] \\ - \frac{1}{2}s_u \cos^2 \psi \{ S - [\Delta^2 s - 2[s, \psi] \tan \psi + [s, d - f + h]] \\ + d_u \{ V - [\Delta^2 h - \frac{1}{4}([d, d] + [\psi, \psi] - [s, s] \cos^2 \psi) \\ + [h, h - f]] \} \} = 0, \quad \dots \dots \dots (11.1)$$

$$\frac{1}{2}\psi_v \{ \Psi - [\Delta^2 \psi - [s, s] \sin \psi \cos \psi + [\psi, d - f + h]] \\ - \frac{1}{2}s_v \cos^2 \psi \{ S - [\Delta^2 s - 2[s, \psi] \tan \psi + [s, d - f + h]] \\ + d_v \{ V - [\Delta^2 h - \frac{1}{4}([d, d] + [\psi, \psi] - [s, s] \cos^2 \psi) \\ + [h, h - f]] \} \} = 0, \quad \dots \dots \dots (11.2)$$

from which the theorem at once follows.

Turning now to the form (2.2) we note that the equations in this case can be obtained from those for (2.1) by setting $f = h = j$. In this case we state the following:—

3. *Theorem II.*—Assume that we have obtained a set (ψ, s, d) which satisfy equations (10) as well as (7.1), (7.2), and (7.3) for the form (2.2). If this set is substituted in (7.5) and (7.6) and (j_u, j_v) computed, then $j_u du + j_v dv$ is

a total differential. j can therefore be computed by a single quadrature, and the (ψ, s, d, j) so obtained will satisfy (7.4) the remaining equation.

If, furthermore, $E=0$ then $\Delta^2 e^d=0$. If ϕ is any function not identically zero such that $\Delta^2 \phi=0$, then it follows by the theory of isometric coordinates in two variables that the coordinate system can be so chosen that $\phi=e^d$. In fact, a condition of this type determines the coordinate system uniquely up to an arbitrary constant.

It may be asked what advantage is gained by adding the two equations (10) to the set (7) as is done in theorems I. and II. Thus theorem I. consists in replacing two equations of the set (7) by equations (10). However, these two equations need not necessarily be interpreted as differential conditions upon the $T^{\mu\nu}$, but rather as conditions which certain functions entering in $T^{\mu\nu}$ must satisfy. Thus in the case of a perfect fluid, they give relations between the pressure and density. These relations can be integrated and the pressure eliminated from (7). In empty space, the equations (10) are necessarily satisfied. In situations such as these, theorem I. reduces the problem to the solution of four simultaneous equations in five unknown functions. A canonicalization of the coordinate system will, if properly chosen, reduce the number of these equations to four. The problem is now of such a form that it can be attacked by the methods of series expansions.

4. A special case of the situation of theorem II. represents a generalization of the theory of Weyl* and Levi-Civita† of the axially symmetric static gravitational field. Just as in Weyl's treatment we shall assume that the internal stresses in matter are zero or so small that they can be neglected, and use

$$T^{\mu\nu} = \rho \frac{dx^\mu}{ds} \frac{dx^\nu}{ds}, \quad . \quad . \quad . \quad . \quad . \quad (12)$$

as the matter energy tensor for the form (2.2). If we omit from consideration the extreme case where $\frac{dx^\Delta}{ds}=0$, it follows that $\frac{dx^{(2)}}{ds} = \frac{dx^{(3)}}{ds} = 0$. The equations (10) in this case give

$$\cos \psi (e^s - k^2 e^{-s}) + 2k \sin \psi = e^{\sigma-d}, \quad . \quad . \quad (13)$$

* Weyl, *Ann. der Phys.* 4te Folge, Band liv. p. 130 (1917).

† Levi-Civita, *Atti della Reale Accademia dei Lincei*, xxxvi. p. 3 (1919).

if $\rho \neq 0$ where σ is a constant. From (8) and (12) it follows that

$$E = 0,$$

$$\Psi = -\rho^x e^{d-\sigma} \{ \sin \psi (e^s - k^2 e^{-s}) - 2k \sin \psi \},$$

$$S = -\rho^x \frac{e^{d-\sigma}}{\cos \psi} \{ e^s + k^2 e^{-s} \},$$

$$V = -\frac{1}{2} \rho^x,$$

$$W = U = 0,$$

where following Weyl $\rho^x = \rho e^{2f}$ will be called the mass density in the canonical coordinate system. Equation (6.3) becomes

$$\Delta^2 e^d = 0, \quad . \quad . \quad . \quad . \quad . \quad (15)$$

so that the coordinate system can be canonicalized making $e^d = u$ as Weyl did, or otherwise if so desired. After having obtained a solution (ψ, s) of equations (7.1) and (7.2) in this case, we can obtain j by a single quadrature.

5. It would obviously be very difficult to obtain exact solutions of the types considered. Approximations by the methods of power series expansions may be obtained. We will mention two types of such expansion:

$$\left. \begin{aligned} \psi &= \psi_1 \rho + \psi_2 \rho^2 + \psi_3 \rho^3 + \dots, \\ s &= s_0 + s_1 \rho + s_2 \rho^2 + \dots, \\ d &= d_0 + d_1 \rho + d_2 \rho^2 + \dots, \\ f &= f_0 + f_1 \rho + f_2 \rho^2 + \dots, \\ h &= h_0 + h_1 \rho + h_2 \rho^2 + \dots, \end{aligned} \right\} . \quad . \quad . \quad . \quad (15)$$

and

$$\left. \begin{aligned} \psi &= \psi_1 \omega + \psi_3 \omega^3 + \psi_5 \omega^5 + \dots, \\ s &= s_0 + s_2 \omega^2 + s_4 \omega^4 + \dots, \\ d &= d_0 + d_2 \omega^2 + d_4 \omega^4 + \dots, \\ f &= f_0 + f_2 \omega^2 + f_4 \omega^4 + \dots, \\ h &= h_0 + h_2 \omega^2 + h_4 \omega^4 + \dots \end{aligned} \right\} . \quad . \quad . \quad (16)$$

For instance, ρ and ω might represent the density and angular velocity respectively of a rotating body.

6. By applying the expansion (15) to the above generalization of the Weyl-Levi-Civita theory, we can obtain a first approximation to the field of a rotating body. The zeroth

approximation corresponds to the Euclidian space for which we shall use the quadratic form

$$ds^2 = dx_0^2 - u^2 dx_1^2 - du^2 - dv^2. \quad (17)$$

This, together with the condition $d_i = 0, (i \neq 0)$ canonicalizes the coordinate system. The equations for ψ_1 and s_1 are

$$\left. \begin{aligned} \frac{\partial^2(\rho\psi_1)}{\partial u^2} + \frac{\partial^2(\rho\psi_1)}{\partial v^2} + \frac{1}{u} \frac{\partial(\rho\psi_1)}{\partial u} - \frac{1}{u^2} \rho\psi_1 &= \frac{2\omega u \rho}{1 - \omega^2 u^2}, \\ \frac{\partial^2(\rho s_1)}{\partial u^2} + \frac{\partial^2(\rho s_1)}{\partial v^2} + \frac{1}{u} \frac{\partial(\rho s_1)}{\partial u} &= \frac{1 + \omega^2 u^2}{1 - \omega^2 u^2} \rho, \end{aligned} \right\} \quad (18)$$

which can be solved by well-known methods when we require that (ψ, s) , together with their first derivatives, be continuous. ρs_1 , in fact, represents the Newtonian potential of an axially symmetric distribution of matter whose density is given by

$$-\frac{1}{4\pi} \frac{1 + \omega^2 u^2}{1 - \omega^2 u^2} \rho.$$

It follows also in this case that $j_1 = -\frac{s_1}{2}$.

7. The expansion (16) can be applied to theorem I. to determine the gravitational field outside of a rotating fluid. Various canonicalizations corresponding to those used by Bach* can be chosen, and Bach's solution obtained by much less labour than is involved when the expansion is applied directly to the Einstein equations as Bach did.

At first sight we might think that here is a method for the determination of the gravitational field of a body of small mass rotating at high angular velocity. However, equations (18) are no longer valid in this case where the internal stresses cannot be neglected. A complete solution, both inside and outside of this interesting case, appears very difficult. On the other hand, it is very easy to obtain a first approximation to the external solution corresponding to any angular velocity, using series (15) where ρ is interpreted as the mass. We shall use for the zeroth approximation the form

$$ds^2 = dx_0^2 - e^{2u} \sin^2 v dx_1^2 - e^{2u} (du^2 + dv^2), \quad (19)$$

giving

$$d_0 = u + \log \sin v,$$

$$s_0 = -u - \log \sin v,$$

$$j_0 = u,$$

* Bach, 'Neue Lösungen der Einsteinschen Gravitationsgleichungen,' A, *Mathematische Zeitschrift*, Band xiii. p. 119 (1922).

while for the first approximation we obtain the equations

$$\left. \begin{aligned} \frac{\partial^2 \psi_1}{\partial u^2} + \frac{\partial^2 \psi_1}{\partial v^2} + \frac{\partial \psi_1}{\partial u} + \frac{\partial \psi_1}{\partial v} \cot v - \psi_1 \cot^2 v &= 0, \\ \frac{\partial^2 s_1}{\partial u^2} + \frac{\partial^2 s_1}{\partial v^2} + \frac{\partial s_1}{\partial u} + \frac{\partial s_1}{\partial v} \cot v + \frac{2\partial d_1}{\partial u} + \frac{2\partial d_1}{\partial v} \cot v &= 0. \end{aligned} \right\} \quad (20)$$

Completing the canonicalization of the coordinate system by setting $d_1 = 0$, we obtain for the general solution

$$\left. \begin{aligned} \psi_1 &= \sum_n^{1-\infty} \psi_{1,n} e^{-nu} P_n^{(1)}(\cos v), \\ s_1 &= \sum_n^{1-\infty} s_{1,n} e^{-nu} P_n(\cos v), \end{aligned} \right\} \quad (21)$$

when we require that ψ_1 and s_1 vanish for $u = \infty$, and that they may be periodic in v . $\psi_{1,n}$, $s_{1,n}$ are constants of integration, and P_n and $P_n^{(1)}$ Legendre polynomials of indices 0 and 1 respectively. It also follows in this case that

$$j_1 = -\frac{s_1}{2}.$$

The second approximation should be carried out without great labour. The series so obtained does not give a good approximation near the origin. An analysis of such a field by a test particle by means of the geodesic equation proves interesting, but will not be attempted here.

In another paper this theory will be applied to the study of the gravitational field of a rotating incompressible fluid.

Berlin,
Feb. 20th, 1929.

XXV. *The Rotating Fluid in the Relativity Theory.*

By EDWARD S. AKELEY *.

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* Communicated by the Author.

Introduction.

THE actual determination of the field of a rotating axially symmetric body has been attacked by both Bach* and Thirring†. Thirring assumed a spherical form, and determined by the method of retarded potentials an approximation to the field in the form of a power-series expansion in the angular velocity. Bach operated directly with the Einstein field equations for empty space, expanding the gravitational potentials in a power series in the angular velocity, in which the zeroth approximation represented the Einstein spherically symmetric solution, while a certain constant of integration was determined by comparison with the Thirring solution. He chose a particular solution out of a discretely infinite set of possible ones.

The author attempted to determine the field both inside and outside a rotating incompressible fluid by using the type of expansion employed by Bach and by applying theorem I. of a previous paper‡. The particular solution corresponding to the one used by Bach was chosen as it gave an approximately ellipsoidal surface. The canonicalization of the coordinate system inside the fluid was effected by requiring that the surfaces of constant pressure be coordinate surfaces, and by specifying the coordinate gradient of pressure. A corresponding type of canonicalization was used outside. These canonicalizations unfortunately introduced singularities in the g_{ij} at the origin and at infinity, making it a very delicate matter to choose solutions which were sufficiently general and which still did not introduce singularities in the natural geometry. However, after this had been done, the number of arbitrary constants was not sufficient to determine a solution so that the g_{ij} and their derivatives would be continuous on the boundary. On the other hand, there were more than enough constants to make the g_{ij} alone continuous. This throws great doubt upon the validity of Bach's solution as the representation of the field of a rotating fluid. A comparison of these solutions with the one actually obtained in this paper suggests that both Bach and the author should have chosen a different particular solution of the equations. Even then, however, there seems to be a question as to the closeness of approximation which is obtained by the series expansions used, particularly when $\frac{\omega^2}{\rho}$ is large.

* Bach, *Math. Zeits.* xiii. p. 119 (1922).

† Thirring, *Phys. Zeits.* xix. p. 204 (1918). Thirring and Lense *ibid.* p. 156 (1918).

‡ Akeley, *supra*, p. 322.

It is felt by the author that the method pursued in this paper is a much more satisfactory mode of attack. A modified form of expansion is used in which the zeroth approximation corresponds to the absence of matter while the first corresponds to the Newtonian theory. It will be shown that there is a one-to-one correspondence, between the forms of equilibrium in the classical and in the relativity theory, of such a type that the equations of the surfaces of constant pressure, and the gradient of pressure, are to a first approximation the same in the two theories. Furthermore, the Newtonian solution is sufficient to determine the Einstein metric to a first approximation. Then the equations for the second approximation will be developed. And finally this theory will be applied to determine the gravitational field, accurate to the second approximations, for the figure of equilibrium corresponding to the Maclaurin ellipsoid.

CHAPTER I.

The General Statement of the Problem.

The notation of the previous paper* will be used throughout. The geometry will be based upon the form (I ; I) of that paper, while the fluid will be defined by the matter energy tensor

$$T^{\mu\nu} = (\rho + p) \frac{dx^\mu}{ds} \frac{dx^\nu}{ds} - pg^{\mu\nu}, \quad . \quad . \quad . \quad (1)$$

where ρ is the density (as defined by Schwarzschild) and p the pressure of the fluid. $\omega = \frac{dx^{(0)}}{dx^{(1)}}$ is the angular velocity. ρ and ω will be assumed constant. From the equations

$$-T^{\mu\nu} = G^{\mu\nu} - \frac{1}{2}g^{\mu\nu}G, \quad . \quad . \quad . \quad (2)$$

it follows that

$$\frac{dx^{(2)}}{ds} = \frac{dx^{(3)}}{ds} = 0,$$

if we exclude the case where

$$\frac{dx^{(0)}}{ds} = \rho + p = 0.$$

The differential identities are now equivalent to the two relations :

$$\left. \begin{aligned} \rho_u + \frac{1}{2}(\rho + p)(\log y)_u &= 0, \\ \rho_v + \frac{1}{2}(\rho + p)(\log y)_v &= 0, \\ y &= A + 2\omega C + \omega^2 B. \end{aligned} \right\} \quad . \quad . \quad . \quad (3)$$

where

* Akeley, *loc. cit.*

We shall assume the following expansion :

$$\left. \begin{aligned} d &= \sum_{\alpha=0}^{\infty} \sum_{\beta=0}^{\infty} d_{\alpha, 2\beta} \rho^{\alpha} \omega^{2\beta}, \\ s &= \sum_{\alpha=0}^{\infty} \sum_{\beta=0}^{\infty} s_{\alpha, 2\beta} \rho^{\alpha} \omega^{2\beta}, \\ j &= \sum_{\alpha=0}^{\infty} \sum_{\beta=0}^{\infty} j_{\alpha, 2\beta} \rho^{\alpha} \omega^{2\beta}, \\ \psi &= \sum_{\alpha=0}^{\infty} \sum_{\beta=0}^{\infty} \psi_{\alpha, 2\beta+1} \rho^{\alpha} \omega^{2\beta+1}, \end{aligned} \right\} \dots \dots (4)$$

after noting that d , s , and j are even functions while ψ is an odd function of ω . By a rearrangement of terms these expansions can be written in the form

$$\left. \begin{aligned} d &= \sum_{\alpha=0}^{\infty} d_{\alpha} \rho^{\alpha}, & \text{where} & & d_{\alpha} &= \sum_{\beta=0}^{\alpha} d_{\alpha-\beta, 2\beta} \left(\frac{\omega^2}{\rho} \right)^{\beta}, \\ s &= \sum_{\alpha=0}^{\infty} s_{\alpha} \rho^{\alpha}, & \text{where} & & s_{\alpha} &= \sum_{\beta=0}^{\alpha} s_{\alpha-\beta, 2\beta} \left(\frac{\omega^2}{\rho} \right)^{\beta}, \\ j &= \sum_{\alpha=0}^{\infty} j_{\alpha} \rho^{\alpha}, & \text{where} & & j_{\alpha} &= \sum_{\beta=0}^{\alpha} j_{\alpha-\beta, 2\beta} \left(\frac{\omega^2}{\rho} \right)^{\beta}, \\ \psi &= \omega \sum_{\alpha=0}^{\infty} \psi_{\alpha} \rho^{\alpha}, & \text{where} & & \psi_{\alpha} &= \sum_{\beta=0}^{\alpha} \psi_{\alpha-\beta, 2\beta+1} \left(\frac{\omega^2}{\rho} \right)^{\beta}. \end{aligned} \right\} (5)$$

We shall further assume that

$$\left. \begin{aligned} d_{0, \alpha} &= 0 \quad (\alpha \neq 0), \\ s_{0, \alpha} &= 0 \quad (\alpha \neq 0), \\ \psi_{0, \alpha} &= 0 \quad (\alpha \neq 0), \\ \psi_{\alpha, 0} &= 0 \quad (\alpha), \end{aligned} \right\} \dots \dots (6)$$

whose interpretation is obvious. The first three state that a fluid of zero density is described by the same quadratic form as empty space, while the fourth states that a non-rotating fluid is described by a form where $g_{01}=0$.

We have the following two sets of equations to consider :

$$\left. \begin{aligned} \Delta^2 \psi - [s, s] \sin \psi \cos \psi + [\psi, d] &= \Psi, \\ \Delta^2 d + [d, d] &= \Delta^2 e^d = E, \\ \Delta^2 s - 2[s, \psi] \tan \psi + [s, d] &= S, \end{aligned} \right\} \dots \dots (7)$$

and

$$\left. \begin{aligned} j_u d_v + j_v d_u &= d_{uv} + \frac{1}{2} d_u d_v - \frac{1}{2} \psi_u \psi_v + \frac{1}{2} s_u s_v \cos^2 \psi, \\ j_u d_u - j_v d_v &= \frac{1}{2} (d_{uu} - d_{vv}) + \frac{1}{4} (d_u^2 - d_v^2) \\ &\quad - \frac{1}{4} (\psi_u^2 - \psi_v^2) + \frac{1}{4} (s_u^2 - s_v^2) \cos^2 \psi, \end{aligned} \right\} \quad (8)$$

together with the equations (3). If the expansions (5) are introduced into these equations, then in each successive approximation outside the zeroth the conditions necessary for the application of theorem II.* will be satisfied. In this way we obtain, in place of the two sets of equations (7) and (8), two systems of sets of equations. The n th system of each will be denoted by (7 n) and (8 n) respectively.

The meridian plane is divided into two regions, R_i and R_e , separated by a closed curve C corresponding to the inside, outside, and bounding surface of the fluid respectively. We seek solutions of equations (7), (8), and (3) such that the g_{ij} or (d, s, j, ψ) and their first derivatives are everywhere, except at infinity, finite, single valued, and continuous†, such that they reduce at infinity to their values for a fluid of zero density, and such that the axis of rotation which is a singularity in the coordinate system is not a singularity in the natural geometry. The latter condition ‡ requires on the axis that

$$e^{j - \frac{1}{2}(d-s)} = \cos \psi. \quad (9)$$

The condition that $p=0$ on C together with the equations (3) are equivalent to an additional surface condition, and in this sense (3) can be considered as determining the bounding curve C .

We shall approximate to this solution by means of the expansion (5), and shall require in each approximation that the above-mentioned boundary conditions are satisfied. If these expansions are applied to the hydrodynamical equations (3) and all terms containing powers of ρ greater than n are omitted, we obtain a condition H_n upon the functions $(s_r, d_r, j_r, \psi_{r-1}) (r \leq n-1)$. $(s_n^{(m)}, d_n^{(m)}, j_n^{(m)}, \psi_{n-1}^{(m)})$ will denote the solution of equations (7 n) and (8 n) under the prescribed boundary conditions when the condition H_m is imposed upon the functions $(s_r, d_r, j_r, \psi_{r-1}) (r \leq n)$.

* *Loc. cit.*

† Sen, *Ann. der Phys.* lxxiii. pp. 365-396 (1924). Lanczos, *Ann. der Phys.* lxxiv. pp. 518-540 (1924).

‡ The author is indebted to Dr. Kornel Lanczos for calling his attention to this point. This may be easily proven by requiring that the ratio of the circumference to the diameter of a small circle enclosing the axis of rotation approach π as the circle shrinks on the axis.

In this case the condition H_m will be said to determine a bounding curve $C_n^{(m)}$ which approximates to C . We shall always seek the n th approximation in the form $((s_r^{(n+1)}, d_r^{(n+1)}, \psi_{r-1}^{n+1}, j_r^{n+1}) (r \leq n))$. When this is done, the Newtonian theory will be associated with the first approximation, and a much more rapid convergence is secured than, for instance, if $(s_r^{(n)}, d_r^{(n)}, \psi_{r-1}^n, j_r^n) (r \leq n)$ denotes the n th approximation. In what follows, $R_{in}^{(m)}$ and $R_{en}^{(m)}$ will refer to the two regions separated by $C_n^{(m)}$, while subscripts i and e will refer to these two regions when it is not necessary to be more specific.

It may be asked why an expansion of type (5) is used. In the first place it unites terms which in problems of physical interest are of the same order of magnitude. But still more important is the following reason:—

Suppose that a solution (ψ, d, s) of equations (7) has been obtained such that these functions and their derivatives are continuous on C . In order that j and j_v as computed from (8) be continuous, it is obviously necessary that $d_{uu} - d_{vv}$ and d_{uv} be continuous, which require that $E=0$ on C , a condition that is to be satisfied. But in order that in every approximation the a_r and their derivatives be continuous, an expansion must be used such that $E=0$ implies $E=0(i)$, a requirement that is satisfied by (5), but not by the double expansion (4).

CHAPTER II.

The Correspondence between the Relativity and the Classical Theory of the Rotating Fluid.

The solution for (7₀) and (8₀),

$$\left. \begin{aligned} d_0 &= \log x, \\ s_0 &= -\log x, \\ j_0 &= 0, \end{aligned} \right\} \quad . \quad . \quad . \quad . \quad (10)$$

corresponding to the form

$$ds^2 = (dx^0)^2 - x^2(dx^{(1)})^2 - dx^2 - dy^2 \quad . \quad . \quad . \quad (11)$$

will be used. An expansion of the hydrodynamical equations (3), together with the condition $p=0$ on C , give

$$\left. \begin{aligned} p_0 &= p_1 = 0, \\ (\rho^2 p_2)_x + \frac{\rho}{2} \left\{ \rho(d_1 + s_1) - \frac{\omega^2}{\rho} x^2 \right\}_x &= 0, \\ (\rho^2 p_2)_y + \frac{\rho}{2} \left\{ \rho(d_1 + s_1) - \frac{\omega^2}{\rho} x^2 \right\}_y &= 0, \end{aligned} \right\} \quad (12)$$

while for s_1 and d_1 we obtain the equations:

$$\left. \begin{aligned} \frac{\partial^2(\rho s_1)}{\partial x^2} + \frac{\partial^2(\rho s_1)}{\partial y^2} + \frac{1}{x} \frac{\partial \rho(s_1 - d_1)}{\partial x} &= \rho, \\ \frac{\partial^2(\rho d_1)}{\partial x^2} + \frac{\partial^2(\rho d_1)}{\partial y^2} + \frac{2}{x} \frac{\partial(\rho d_1)}{\partial x} &= 0, \end{aligned} \right\} \quad (\text{Ri}) \quad (13)$$

and

$$\left. \begin{aligned} \frac{\partial^2 s_1}{\partial x^2} + \frac{\partial^2 s_1}{\partial y^2} + \frac{1}{x} \frac{\partial(s_1 - d_1)}{\partial x} &= 0, \\ \frac{\partial^2 d_1}{\partial x^2} + \frac{\partial^2 d_1}{\partial y^2} + \frac{2}{x} \frac{\partial d_1}{\partial x} &= 0. \end{aligned} \right\} \quad (\text{Re}) \quad (14)$$

The coordinate system can be so canonicalized that $d_{1,\epsilon}^{(2)} = 0$. Then it follows that $d_{1,i}^{(2)} = 0$. A comparison of equations (12), (13), and (14) with those of the classical* theory reveals that if V is the Newtonian potential function of the rotating fluid of density† ρ in the coordinates here specified,

$$\rho s_1^{(2)} = -2V, \quad . \quad . \quad . \quad . \quad . \quad (15)$$

while equations (11), where $\rho^2 p_2$ is treated as the pressure, are the hydrodynamical equations of the classical theory for the rotating fluid. In particular it follows to a first approximation that the surfaces of constant pressure, the gradient of pressure, and the possible figures of equilibrium are the same in the two theories. The equations (8₁) give

$$\rho j_1^{(2)} = -\frac{\rho}{2} s_1^{(2)} = V, \quad . \quad . \quad . \quad . \quad . \quad (16)$$

so that $j_1^{(2)} - \frac{1}{2}(d_1^{(2)} - s_1^{(2)}) = 0$ on the axis, and therefore to a first approximation the singularity condition (9) is satisfied.

It might be noted that while the fluid has been assumed incompressible, the results of this chapter follow almost as simply if no other restriction except axial symmetry is imposed upon the density function.

* Lamb, 'Hydrodynamics,' Chapter 12.

† Account must necessarily be taken of the different units used for ρ in the two theories.

CHAPTER III.

 The Gravitational Field of a Rotating Fluid—
Second Approximation.

Having chosen a particular possible figure of equilibrium of the classical theory, the developments of the previous chapter make it possible to determine the $(d_1^{(2)}, s_1^{(2)}, j_1^{(2)})$ of the corresponding figure in the relativity theory. We shall assume that this has been done, and proceed to the determination of the corresponding $(d_1^{(3)}, s_1^{(3)}, j_1^{(3)}, d_2^{(3)}, s_2^{(3)}, \psi_1^{(3)}, j_2^{(3)})$.

The equations (8), when referred to the form (10) as the zeroth approximation, give for the second approximation

$$\left. \begin{aligned} [j_2 - \frac{1}{2}(d_2 - s_2)]_x &= \frac{x}{2}(d_{2xx} - d_{xxy}) + \frac{x}{4}(s_{1x}^2 - s_{1y}^2), \\ [j_2 - \frac{1}{2}(d_2 - s_2)]_y &= x d_{2xy} + \frac{x}{2} s_{1x} s_{1y}. \end{aligned} \right\} \quad (8_2)$$

It follows at once that $j_2 - \frac{1}{2}(d_2 - s_2)$ is constant on the axis $x=0$. Since $j_2^{(3)}$, $s_2^{(3)}$, and $d_2^{(3)}$ are chosen to vanish at infinity, $j_2^{(3)} - \frac{1}{2}(d_2^{(3)} - s_2^{(3)})$ also vanishes on the axis, and the singularity condition (9) is satisfied. Furthermore, as soon as $(s_2^{(3)}, d_2^{(3)})$ and $(s_1^{(3)}, d_1^{(3)})$ are known, $j_2^{(3)}$ can be obtained from (8₂) by a single integration.

It remains to determine $(d_1^{(3)}, s_1^{(3)}, j_1^{(3)}, d_2^{(3)}, s_2^{(3)}, \psi_1^{(3)})$. Equation (3) can be integrated, giving

$$\rho + p = \frac{q}{\sqrt{\gamma}}, \quad . \quad . \quad . \quad . \quad . \quad (17)$$

where q is a constant of integration subject to an expansion of type (5), and

$$\left. \begin{aligned} q_0 &= 0, \\ q_1 &= 1, \quad (R_i) \\ q_1 &= 0. \quad (R_e) \end{aligned} \right\} \quad . \quad . \quad . \quad . \quad . \quad (18)$$

From (17) we obtain for $C_2^{(2)}$ the condition

$$\frac{\omega^2}{\rho} e^{-2s_0} - a_1^{(2)} + 2q_2 = 0, \quad . \quad . \quad . \quad . \quad . \quad (19)$$

and for $C_3^{(3)}$ the condition

$$\begin{aligned} q_2 - \frac{1}{2} a_1^{(3)} + \frac{1}{2} \frac{\omega^2}{\rho} e^{-2s_0} + \rho \left\{ q_3 - \frac{1}{2} a_2^{(3)} - \frac{1}{2} q_2 a_1^{(3)} + \frac{1}{8} (a_1^{(3)})^2 \right. \\ \left. - \frac{\omega^2}{\rho} (s_1^{(3)} e^{-2s_0} + \psi_1^{(3)} e^{-s_0}) + \frac{1}{8} \frac{\omega^4}{\rho^2} e^{-4s_0} \right\} = 0, \quad . \quad (20) \end{aligned}$$

where $a = d + s$.

Equations (7₂) are in this case equivalent to the following :

$$\left. \begin{aligned} \Delta\psi_1 + [\psi_1, d_0] - \psi_1[s_0, s_0] &= -2q_1 e^{2j_0 - s_0}, \\ \Delta d_2 + 2[d_2, d_0] &= q_1 e^{2j_0} \left[2q_2 - a_1 + \frac{\omega^2}{\rho} e^{-4s_0} \right], \\ \Delta a_2 + [a_2, d_0] &= q_1 e^{2j_0} \left[3q_2 - \frac{5}{2}a_1 + \frac{7}{2} \frac{\omega^2}{\rho} e^{-4s_0} \right], \end{aligned} \right\} \quad (21)$$

equations which are valid for both R_ϵ and R_i when due account of (18) is taken.

We shall assume that the coordinate system has been so chosen that the equation of $C_2^{(2)}$ is $u = u_0$ a constant, and that the solution $(a_1^{(2)}, d_1^{(2)}, j_1^{(2)}, \psi_1^{(2)}, d_2^{(2)}, a_2^{(2)}, j_2^{(2)})$ has been obtained by well-known methods. The solution $(a_1^{(3)}, d_1^{(3)}, j_1^{(3)}, \psi_1^{(3)}, d_2^{(3)}, a_2^{(3)}, j_2^{(3)})$ will be determined by the method of perturbations as follows:—If $\rho \bar{a}_1^{(2)}$ and $\rho \bar{a}_1^{(2)}$ denote the increments which must be added to the solutions of the equations for d_1 and a_1 respectively when $C_3^{(3)}$ instead of $C_2^{(2)}$ is considered as the bounding curve, then

$$\left. \begin{aligned} d_1^{(3)} &= d_1^{(2)}, \\ a_1^{(3)} &= a_1^{(2)}, \\ \psi_1^{(3)} &= \psi_1^{(2)}, \\ d_2^{(3)} &= d_2^{(2)} + \bar{d}_1^{(2)}, \\ a_2^{(3)} &= a_2^{(2)} + \bar{a}_1^{(2)}. \end{aligned} \right\} \quad (22)$$

Let $\phi_{a,i}$ and $\phi_{a,\epsilon}$ be the characteristic functions of the equations for a_1 which are finite in R_i and R_ϵ respectively, and seek to obtain $\bar{a}_1^{(2)}$ in the form

$$\left. \begin{aligned} \bar{a}_{1,\epsilon}^{(2)} &= \sum_{\alpha=1}^n A_{\alpha,\epsilon} \phi_{\alpha,\epsilon}, \\ \bar{a}_{1,i}^{(2)} &= \sum_{\alpha=1}^n A_{\alpha,i} \phi_{\alpha,i}. \end{aligned} \right\} \quad (23)$$

If the equation of $C_3^{(3)}$ is written in the form

$$u = u_0 + \rho u_1, \quad (24)$$

where u_1 is a function of v , then

$$\sum_{\alpha=1}^n A_{\alpha,\epsilon} \phi_{\alpha,\epsilon} = \sum_{\alpha=1}^n A_{\alpha,i} \phi_{\alpha,i} \quad (u = u_0), \quad (25.1)$$

$$\sum_{\alpha=1}^n A_{\alpha, \epsilon} \frac{\partial \phi_{\alpha, \epsilon}}{\partial u} = \sum_{\alpha=1}^n A_{\alpha, i} \frac{\partial \phi_{\alpha, i}}{\partial u} + u_1 \left(\frac{\partial^2 a_{1, i}}{\partial u^2} - \frac{\partial^2 a_{1, \epsilon}}{\partial u^2} \right) \quad (u = u_0),$$

$$\dots \dots \dots (25.2)$$

$$q' + \frac{u_1}{2} \left(\frac{\omega^2}{\rho} \frac{\partial e^{-2s_0}}{\partial u} - \frac{\partial a_1^{(3)}}{\partial u} \right) - \frac{1}{2} a_2^{(2)} + q_1 (a_1^{(2)})^2 - \frac{1}{2} q_2 a_1^{(2)}$$

$$- \frac{\omega^2}{\rho} (s_1^{(2)} e^{-2s_0} + \psi_1^{(2)} e^{-s_0}) + \frac{1}{8} \frac{\omega^4}{\rho^2} e^{-4s_0}$$

$$= \frac{1}{2} \bar{a}_1^{(2)} \quad (u = u_0), \quad (25.3)$$

where q' is a new constant of integration, must be identities in r . u_1 can first be eliminated between (25.2) and (25.3). The resulting identity together with (25.1) will determine the constants $A_{\alpha, \epsilon}$, $A_{\alpha, i}$, and q' . Then u_1 can be determined from (25.2).

When we carry out a corresponding process for $\bar{d}_1^{(2)}$, it follows that $\bar{d}_1^{(2)} = 0$, since

$$\frac{\partial^2 (d_{1, i} - d_{1, \epsilon})}{\partial u^2} = 0 \quad (u = u_0).$$

CHAPTER IV.

The Maclaurin Ellipsoid in the Relativity Theory.

For the zeroth approximation we shall use the quadratic form

$$ds^2 = (dx^0)^2 - k^2 \cosh^2 \eta \sin^2 \theta (dx^{(1)})^2$$

$$- \frac{k^2}{2} (\cosh 2\eta + \cos 2\theta) (d\eta^2 + d\theta^2), \quad (26)$$

which can be obtained from the form (11) by the transformation

$$\left. \begin{aligned} x &= k \cosh \eta \sin \theta, \\ y &= k \sinh \eta \cos \theta. \end{aligned} \right\} \dots \dots \dots (27)$$

It should be noted that in coordinate transformations of the type (27) e^{2j_0} transforms as a tensor, while ψ_α , d_α , s_α , and $j_\beta(\alpha)(\beta \neq 0)$ transform as scalars. It will therefore not be considered necessary always to transform the results to the elliptic coordinates represented by the form (26). In this connexion the notation used in Lamb's 'Hydrodynamics,' Chapter 12, will be adopted with the single modification that $(2a, 2b)$ instead of $(2a, 2c)$ will represent the major and minor axes of the bounding curve $C_2^{(2)}$.

From (26) we obtain

$$\left. \begin{aligned} d_0 &= \log k + \log \cosh \eta + \log \sin \theta, \\ s_0 &= -\log k - \log \cosh \eta - \log \sin \theta, \\ j_0 &= \log \frac{k}{\sqrt{2}} + \frac{1}{2} \log (\cosh 2\eta + \cos 2\theta). \end{aligned} \right\} \quad (28)$$

The first approximation can at once be written down from the classical theory and the results of Chapter 2, namely

$$\left. \begin{aligned} d_{1,i}^{(2)} &= 0, \\ s_{1,i}^{(2)} &= \frac{1}{4} \{ k^2 \alpha_0 \cosh^2 \eta \sin^2 \theta + k^2 \beta_0 \sinh^2 \eta \cos^2 \theta - \chi_0 \}, \\ j_{1,i}^{(2)} &= -\frac{s_{1,i}^{(2)}}{2}, \end{aligned} \right\} \quad (29)$$

where

$$\left. \begin{aligned} \alpha_0 &= \zeta_0 (1 + \zeta_0^2) \cot^{-1} \zeta_0 - \zeta_0^2, \\ \beta_0 &= 2(1 + \zeta_0^2) [1 - \zeta_0 \cot^{-1} \zeta_0], \\ \chi_0 &= 2k^2 \zeta_0 (1 + \zeta_0^2) \cot^{-1} \zeta_0, \end{aligned} \right\} \quad (30)$$

and

$$\left. \begin{aligned} d_{1,\epsilon}^{(2)} &= 0, \\ s_{1,\epsilon}^{(2)} &= \frac{1}{4} \int_{\lambda}^{\infty} \left\{ \frac{x^2}{a^2 + \lambda} + \frac{y^2 - 1}{b^2 + \lambda} \right\} \frac{d\lambda}{(a^2 + \lambda) \sqrt{b^2 + \lambda}}, \\ j_{1,\epsilon}^{(2)} &= -\frac{s_{1,\epsilon}^{(2)}}{2}, \end{aligned} \right\} \quad (31)$$

where λ is a root of

$$\frac{x^2}{a^2 + \lambda} + \frac{y^2}{b^2 + \lambda} = 1. \quad (32)$$

The equation of $C_2^{(2)}$ is

$$\frac{\omega^2}{\rho} e^{-2s_0} - \alpha_i^{(2)} + 2q_2 = 0, \quad (33)$$

and from (28), (29), and (33) it follows that

$$k^2 \left(\alpha_0 - \frac{4\omega^2}{\rho} \cosh^2 \eta \sin^2 \theta + k^2 \beta_0 \sinh^2 \eta \cos^2 \theta \right) = 8q_2 + \chi_0 \quad (34)$$

represents the surface of the fluid. In order that this shall coincide with the ellipse $\eta = \eta_0$, (34) must be an identity in θ when $\eta = \eta_0$. We obtain in this way

$$\frac{4\omega^2}{\rho} = \zeta_0 (1 + 3\zeta_0^2) \cot^{-1} \zeta_0 - 3\zeta_0^2, \quad (35)$$

$$q_2 + \frac{\chi_0}{8} = \frac{1}{4} k^2 \xi_0^2 (1 + \xi_0^2) [1 - \xi_0 \cot^{-1} \xi_0], \quad (36)$$

(35) being the well-known equation associated with the Maclaurin ellipsoid.

The equations for (ψ_1, d_2, a_2) , referred to the form (26) as the zeroth approximation, are :

$$\frac{\partial^2 \psi_1}{\partial \eta^2} + \frac{\partial^2 \psi_1}{\partial \theta^2} + \frac{\partial \psi_1}{\partial \eta} \tanh \eta + \frac{\partial \psi_1}{\partial \theta} \cot \theta - \psi_1 [\tanh^2 \eta + \cot^2 \theta] = -q_1 k^3 (\cosh 2\eta + \cos 2\theta), \quad (37.1)$$

$$\begin{aligned} \frac{\partial^2 d_2}{\partial \eta^2} + \frac{\partial^2 d_2}{\partial \theta^2} + 2 \frac{\partial d_2}{\partial \eta} \tanh \eta + 2 \frac{\partial d_2}{\partial \theta} \cot \theta \\ = + q_1 \frac{k^2}{2} (\cosh 2\eta + \cos 2\theta) \left[2q_2 - a_1 + \frac{\omega^2}{\rho} k^2 \cosh^2 \eta \sin^2 \theta \right], \end{aligned} \quad (37.2)$$

$$\begin{aligned} \frac{\partial^2 a_2}{\partial \eta^2} + \frac{\partial^2 a_2}{\partial \theta^2} + \frac{\partial a_2}{\partial \eta} \tanh \eta + \frac{\partial a_2}{\partial \theta} \cot \theta \\ = q_1 \frac{k^2}{2} (\cosh 2\eta + \cos 2\theta) \left[3q_2 - \frac{5}{2} a_1 + \frac{7}{2} \frac{\omega^2}{\rho} k^2 \cosh^2 \eta \sin^2 \theta \right]. \end{aligned} \quad (37.3)$$

The solution $\psi_1^{(2)}$ is unique under the specified boundary conditions. In fact, it is easy to show that

$$\begin{aligned} \psi_{1,i}^{(3)} = \psi_{1,i}^{(2)} = P_3^{(1)}(\mu) \left\{ \psi_{1,i3} \frac{P_3^{(1)}(i\xi)}{P_3^{(1)}(i\xi_0)} + \frac{2k^3}{75} P_1^{(1)}(i\xi) \right\} \\ + P_1^{(1)}(\mu) \left\{ \frac{2k^3}{75} P_3^{(1)}(i\xi) + \psi_{1,i1} \frac{P_1^{(1)}(i\xi)}{P_1^{(1)}(i\xi_0)} \right\}, \end{aligned} \quad (38.1)$$

$$\begin{aligned} \psi_{1,\epsilon}^{(3)} = \psi_{1,\epsilon}^{(2)} = \psi_{1,\epsilon3} P_3^{(1)}(\mu) \frac{Q_3^{(1)}(i\xi)}{Q_3^{(1)}(i\xi_0)} + \psi_{1,\epsilon1} P_1^{(1)}(\mu) \frac{Q_1^{(1)}(i\xi)}{Q_1^{(1)}(i\xi_0)}, \\ \quad \quad \quad (38.2) \end{aligned}$$

where $P_n^{(m)}$ and $Q_n^{(m)}$ are the well-known associated Legendre polynomials and $i = \sqrt{-1}$. When ψ_1 and $\frac{\partial \psi_1}{\partial n}$ are required to be continuous at $C_2^{(2)}$, the constants of integration $\psi_{1,in}$ and $\psi_{1,\epsilon n}(n)$ are determined by the pairs of simultaneous algebraic equations :

$$\left. \begin{aligned} \psi_{1,\epsilon3} - \psi_{1,i3} &= \frac{2}{75} P_1^{(1)}(i\xi_0), \\ \psi_{1,\epsilon3} \frac{Q_3^{(2)}(i\xi_0)}{Q_3^{(1)}(i\xi_0)} - \psi_{1,i3} \frac{P_3^{(2)}(i\xi_0)}{P_3^{(1)}(i\xi_0)} &= \frac{2}{75} P_1^{(2)}(i\xi_0), \end{aligned} \right\} \quad (39)$$

$$\left. \begin{aligned} \psi_{1, \epsilon 1} - \psi_{1, i 1} &= \frac{2}{75} P_3^{(1)}(i\xi_0), \\ \psi_{1, \epsilon 1} \frac{Q_1^{(2)}(i\xi_0)}{Q_1^{(1)}(i\xi_0)} - \psi_{1, i 1} \frac{P_1^{(2)}(i\xi_0)}{P_1^{(1)}(i\xi_0)} &= \frac{2}{75} P_3^{(2)}(i\xi_0). \end{aligned} \right\} \quad (40)$$

The solution $d_2^{(3)} = d_2^{(2)}$ is unique so soon as the coordinate system is canonicalized by setting $d_{2, \epsilon}^{(2)} = 0$. Then we obtain

$$\begin{aligned} d_{2, i}^{(3)} = & S_5(\theta) \{ d_{2, i5} \text{Ch}_5(\eta) - l_d \text{Ch}_3(\eta) + m_d \text{Ch}_1(\eta) + \delta_{2, i5} \text{Sh}_5(\eta) \} \\ & + S_3(\theta) \{ l_d \text{Ch}_5(\eta) + d_{2, i3} \text{Ch}_3(\eta) - n_d \text{Ch}_1(\eta) + \delta_{2, i3} \text{Sh}_3(\eta) \} \\ & + S_1(\theta) \{ m_d \text{Ch}_5(\eta) + n_d \text{Ch}_3(\eta) + \delta_{2, i1} \text{Ch}_1(\eta) + \delta_{2, i1} \text{Sh}_1(\eta) \}, \end{aligned} \quad (41)$$

where

$$\text{Ch}_n(\theta) = \frac{\cosh n\theta}{\cosh \theta}, \quad \text{Sh}_n(\theta) = \frac{\sinh n\theta}{\cosh \theta}, \quad \text{and} \quad S_n(\theta) = \frac{\sin n\theta}{\sin \theta},$$

and where the constants (l_d , m_d , n_d) are defined by the equations:

$$\left. \begin{aligned} l_d &= -\frac{k^4}{3 \cdot 7^2} \left\{ \frac{28}{5} \frac{\omega^2}{\rho} + \beta_0 - \alpha_0 \right\}, \\ m_d &= \frac{k^4}{3 \cdot 4 \cdot 5 \cdot 7} \left\{ 2\alpha_0 - \beta_0 - \frac{56}{5} \frac{\omega^2}{\rho} \right\}, \\ n_d &= -\frac{k^4}{2^3 \cdot 3^2 \cdot 7} \left\{ 3\beta_0 - 8\alpha_0 + \frac{224}{5} \frac{\omega^2}{\rho} \right\} - \frac{k^2}{9} (3q_2 + \frac{5}{8}\chi_0). \end{aligned} \right\} \quad (42)$$

The solution $a_2^{(2)}$ of (37.3) is also unique:

$$\begin{aligned} a_{2, i}^{(2)} = & P_4(\mu) \left\{ a_{2, i4}^{(2)} \frac{P_4(i\xi)}{P_4(i\xi_0)} + l_a P_2(i\xi) + m_a \right\} \\ & + P_2(\mu) \{ l_a P_4(i\xi) + a_{2, i2}^{(2)} P_2(i\xi) + n_a \} \\ & + P_0(\mu) \{ m_a P_4(i\xi) + n_a P_2(i\xi) + a_{2, i0}^{(2)} \}, \end{aligned} \quad (46.1)$$

$$a_{2, \epsilon}^{(2)} = a_{2, \epsilon 4}^{(2)} P_4(\mu) Q_4(i\xi) + a_{2, \epsilon 2}^{(2)} P_2(\mu) Q_2(i\xi) + a_{2, \epsilon 0}^{(2)} Q_0(i\xi), \quad (46.2)$$

where the constants (l , m , n) are defined by the equations:

$$\left. \begin{aligned} l_a &= -\frac{k^4}{16 \cdot 256} \left\{ \frac{4\omega^2}{\rho} - \alpha_0 + \beta_0 \right\}, \\ m_a &= \frac{k^4}{24 \cdot 256} \left\{ \frac{12\omega^2}{\rho} - 3\alpha_0 - \beta_0 \right\}, \\ n_a &= \frac{k^4}{16 \cdot 256} \left\{ \frac{4\omega^2}{\rho} - \alpha_0 + 2\beta_0 \right\} + \frac{k^2}{128} (8q_2 + \chi_0). \end{aligned} \right\} \quad (47)$$

Again, when $d_2^{(2)}$, $\frac{\partial d_2^{(2)}}{\partial \eta}$, $a_2^{(2)}$, and $\frac{\partial a_2^{(2)}}{\partial \eta}$ are required to be continuous at $C_2^{(2)}$, the constants of integration ($d_{2, \epsilon m}$, $d_{2, im}$) and ($\alpha_{2, \epsilon m}$, $\alpha_{2, im}$) are determined by pairs of simultaneous algebraic equations, similar to (39) and (40), which it is hardly necessary to write down.

There remains the computation of $\bar{a}_1^{(2)}$. We shall assume the expansion

$$\left. \begin{aligned} \alpha_{1, \epsilon}^{(2)} &= \bar{a}_{1, 4}^{(2)} P_4(\mu) \frac{Q_4(i\zeta)}{Q_4(i\zeta_0)} + \bar{a}_{1, 2}^{(2)} P_2(\mu) \frac{Q_2(i\zeta)}{Q_2(i\zeta_0)} + \bar{a}_{1, 0}^{(2)} \frac{Q_0(i\zeta)}{Q_0(i\zeta_0)}, \\ \bar{a}_{1, i}^{(2)} &= \bar{a}_{1, 4}^{(2)} P_4(\mu) \frac{P_4(i\zeta)}{P_4(i\zeta_0)} + \bar{a}_{1, 2}^{(2)} P_2(\mu) \frac{P_2(i\zeta)}{P_2(i\zeta_0)} + \bar{a}_{1, 0}^{(2)}, \end{aligned} \right\} \dots (50)$$

satisfying (25.1). Eliminating from (25.2) and (25.3), noting that

$$\frac{\partial^2 a_{1, \epsilon}}{\partial \eta^2} - \frac{\partial^2 a_{1, \epsilon}}{\partial \eta^2} = e^{2j_0} (\eta = \eta_0),$$

substituting in the values of j_0 , $\bar{a}_1^{(2)}$, s_0 , and d_0 already obtained, and then noting that the resulting equation is an identity in θ for $\eta = \eta_0$, we obtain the following equations for the successive determination of $\bar{a}_{1, n}^{(2)}$ and q' :

$$\bar{a}_{1, 4}^{(2)} K_4 = \frac{3}{5} M_6,$$

$$\bar{a}_{1, 2}^{(2)} K_2 = \frac{2}{3} M_4 + \frac{1}{2} \bar{a}_{1, 4}^{(2)} (30K_4 - 35L_4),$$

$$q'(\zeta_0^2 - 1) = M_0 - M_2 - \frac{3}{8} \bar{a}_{1, 4}^{(2)} L_4 + \frac{1}{2} \bar{a}_{1, 2}^{(2)} L_2,$$

$$\bar{a}_{1, 0}^{(2)} K_0 = M_0 - q' \zeta_0^2 - \frac{3}{8} \bar{a}_{1, 4}^{(2)} L_4 + \frac{1}{2} \bar{a}_{1, 2}^{(2)} L_2,$$

where

$$K_n = -\frac{1}{2} + \frac{1}{8} \left\{ \frac{Q_n'(i\zeta_0)}{Q_n(i\zeta_0)} - \frac{P_n'(i\zeta_0)}{P_n(i\zeta_0)} \right\} \left(\alpha_0 - \beta_0 - \frac{4\omega^2}{\rho} \right) \sinh 2\eta_0,$$

$$L_n = -\frac{\zeta_0^2}{2} + \frac{1}{8} \left\{ \frac{Q_n'(i\zeta_0)}{Q_n(i\zeta_0)} - \frac{P_n'(i\zeta_0)}{P_n(i\zeta_0)} \right\} \left(\frac{4\omega^2}{\rho} - \alpha_0 \right) \sinh 2\eta_0,$$

and

$$M_6 \cos^6 \theta + M_4 \cos^4 \theta + M_2 \cos^2 \theta + M_0$$

$$= \left[\frac{1}{2} a_2^{(2)} - q_1 (a_1^{(2)})^2 + \frac{1}{2} q_2 a_1^{(2)} + \frac{\omega^2}{\rho} (s_1^{(2)} e^{-2s_0} + \psi_1^{(2)} e^{-2s_0}) \right.$$

$$\left. - \frac{1}{8} \frac{\omega^4}{\rho^2} e^{-4s_0} \right] [\zeta_0^2 + \cos^2 \theta] \eta = \eta_0.$$

From (25.2) we obtain

$$\eta_1(\xi_0^2 + \mu) = \bar{a}_{1,4}^{(2)} P_4(\mu) \left\{ \frac{Q_4'(i\xi_0)}{P_4(i\xi_0)} - \frac{P_4'(i\xi_0)}{P_4(i\xi_0)} \right\} \\ + \bar{a}_{1,2}^{(2)} P_2(\mu) \left\{ \frac{Q_2'(i\xi_0)}{Q_2(i\xi_0)} - \frac{P_2'(i\xi_0)}{P_2(i\xi_0)} \right\} + a_{1,0}^{(2)} \frac{Q_0'(i\xi_0)}{Q_0(i\xi_0)}. \quad (53)$$

This completes the determination of

$$\psi_1^{(3)}, d_2^{(3)}, a_2^{(3)} = a_2^{(2)} + a_1^{(2)}$$

and the bounding curve

$$C_3^{(3)}: \eta = \eta_0 + \rho\eta.$$

For the determination of $j_2^{(3)}$ it is more convenient to refer to the form (11) as the zeroth approximation. From (8₂) and (41.2) we obtain

$$j_{2,e}^{(3)} = \frac{1}{2}(d_{2,e}^{(3)} - s_{2,e}^{(3)}) + \phi, \quad . \quad . \quad . \quad (54)$$

where

$$\left. \begin{aligned} \phi_x &= \frac{\chi}{4} (s_{1x^2} - s_{1y^2}), \\ \phi_y &= \frac{\chi}{2} s_{1x}s_{1y}, \end{aligned} \right\} . \quad . \quad . \quad . \quad (55)$$

the constant of integration being so chosen that $\phi = 0$ at infinity. The exact solution of these equations is not known. Nevertheless, it is possible to obtain an approximation in the form of a series expansion in functions of ξ_0 .

It is possible to integrate the equations for $j_{2,i}^{(3)}$, and we obtain

$$j_{2,i}^{(3)} = \frac{1}{2}(d_{2,i}^{(3)} - s_{2,i}^{(3)}) + x d_{2,ix}^{(3)} - \left(q_2 + \frac{\chi_0}{8} \right) \frac{x^2}{2} \\ + \left(3\alpha_0 + 2\alpha_0^2 - \frac{12\omega^2}{\rho} \right) \frac{x^4}{96} + \frac{1}{16} \alpha_0 \beta_0 x^2 y^2. \quad (56)$$

In another paper the solution which has been obtained will be applied to the study of phenomena associated with the rotation of the earth.

In conclusion, the author wishes to thank Professor Arthur C. Lunn for the great interest which he took in the earlier part of the investigation, and also Professor Max von Laue and Dr. Kornel Lanczos for their suggestions in the later part of the investigation.

New York,
Nov. 30, 1930.

XXVI. *Impulse Functions.* By W. E. SUMPNER, D.Sc.,
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1. IMPULSIVE QUANTITIES.

THE idea of an impulsive quantity is very old, though such quantities have been little used except by Heaviside, and, so far as I am aware, they have never been formulated. The main idea is clear from the oldest example in mechanics. An "impulsive force" F is stated to produce a finite change of momentum during an infinitesimal time c . The wording used is, in general, rather loose. An impulsive force can differ only in magnitude from an ordinary force, but the phrase is not used to denote a force at all, but the impulse caused by it; and in all physical examples this is a quantity which differs in nature from the force itself. F is supposed to be zero for all values of t except for the range $0 < t < c$; so that if we regard F as the derivative of V we have

$$F = \frac{dV}{dt} \quad \text{and} \quad \int_{-\infty}^{+\infty} F dt = \int_0^c F dt = V_2 - V_1, \quad (1)$$

where V_2 and V_1 are the constant values of V for the ranges $-\infty < t < 0$ and $c < t < \infty$ respectively. Heaviside assumed such a function V with $V_1 = 0$ and $V_2 = 1$, but he did not formulate it, and necessarily assumed that it had some definite value for each infinitesimal value of t . It naturally suggests one of Fourier's series and the integral representing the sum of this series. This integral, with the limits as finally given by Fourier, is not such as to be calculable for infinitesimal values of the variable, and for such values it is usually assumed that the function is discontinuous. Reference to Fourier's original work will, however, show that he only considered finite values of the variable, and that

* Communicated by the Author.

for such values he was entitled to alter the natural limits of the integral, which are c and nc , to 0 and ∞ . By doing this he took away from his integral its innate power of representing the function for infinitesimals. Directly the true limits are restored the value of the integral can easily be calculated for such values. For present purposes we shall only need a very simple case of Fourier's theorem, and in order to keep the sequence clear some comments on the application to infinitesimals of the general theorem are postponed, and form an appendix.

2. HEAVISIDE'S "UNIT" AND IMPULSE FUNCTIONS.

It is the aim of the present paper to formulate and to justify a function such as Heaviside assumed to exist. It may be well to state at once the result of the search for this function. This can be put as follows:—

Definition of the Numbers c , n , and w . (2 a)

Let c be a positive infinitesimal which may be as small as we please, but which, once chosen, must be treated throughout analysis as a fixed quantity.

Let n be a positive integer, chosen after c has been fixed, and so large that nc^2 is infinite.

Let w be a positive infinity, but one of lower order than $1/c$, and such that cw is infinitesimal.

Definition of the "Unit" and Impulse Functions. (2 b)

Define the "unit" function as

$$H(t) \equiv \frac{t^c}{c!} H_{01}(t) \equiv \frac{t^c}{c!} \left[\frac{1}{2} + \frac{1}{\pi} \text{Si}(nct) \right]$$

the derivative of this is the impulse function

$$p H(t) \equiv \frac{d}{dt} H(t).$$

Properties of $H(t)$.

For all values of t between $\pm w$, $H(t)$, and also each of its derivatives pH , p^2H , &c., will be real, single valued, continuous, and perfectly explicit in terms of t , c , and n . H itself consists of an infinite convergent series of power terms in t , the indices of which, except for the first term, will be of type $m+c$ where m is a positive odd integer. (2.1)

For every negative value of t from $-w$ up to and including absolute zero, H will be zero except for a quantity which is highly infinitesimal compared with c (2.2)

For all values of t between 0 and c , H will be either finite or infinitesimal, and will be zero at $t=0$, and unity at $t=c$ (2.3)

For every value of t from $+c$ to $+w$, H will be unity, except for a quantity which is highly infinitesimal compared with c (2.4)

$H(t)$ is a wave function, of constant wave-length, which fluctuates about two level values, these being unity for positive and zero for negative values of t . Its derivative pH is a wave function, of the same wave-length, fluctuating about zero for all values of t (2.5)

3. THE IMPULSE ASPECT OF FOURIER'S THEOREM.

We shall find that, in order to justify the properties of H , it will be necessary to rely upon Fourier's theorem. The assumption of these properties thus involves that of the truth of the theorem, so that H can be regarded as a condensed form of the theorem, one which the latter can take when applied to infinitesimals. It is thus not surprising to find that Heaviside, by assuming $H(t)$, was able easily to establish and to express the theorem in any of its usual forms.

It is obvious that $H(t-x)$, where x is a special value of t , has the same properties for a given value of $(t-x)$ that $H(t)$ has for the same value of t . By assuming the above properties we have (neglecting infinitesimals)

$$\int_{-w}^{+w} pH(t)dt = \int_0^c pH(t)dt = 1,$$

and

$$\int_{-w}^{+w} pH(t-x)dt = \int_x^{x+c} pH(t-x)dt = 1,$$

since

$$\int_{t_1}^{t_1+\partial t} pH(t)dt = 0 = \int_{t_1}^{t_1+\partial t} pH(t-x)dt, \quad . \quad (3.1)$$

for any range ∂t , provided that t , as it increases from t_1 to $t_1+\partial t$, does not pass through zero in the first case or through x in the second case.

Now in any ordinary case of a function of t denoted by $\phi(t)$ we have for any infinitesimal element ∂t

$$\int_{t_1}^{t_1+\partial t} \phi(t) p H(t-x) dt = \phi(t_1) \int_{t_1}^{t_1+\partial t} p H(t-x) dt, \quad (3.2)$$

and thus will be zero unless t passes through x . If $\phi(t)$ is discontinuous at some point in the range the modification needed can easily be made, and the result will be found unaffected unless we are dealing with some portion of the impulse range $x < t < x+c$. If $\phi(t)$ becomes infinite during the range we have a contest between $\phi(t)$ and $p H(t-x)$. The latter factor wins owing to an extraordinary property of $H(t)$ which has yet to be established. Leaving aside such cases, we have

$$\begin{aligned} \int_{-w}^{+w} \phi(t) p \cdot H(t-x) dt &= \int_x^{x+c} \phi(t) p \cdot H(t-x) dt \\ &= \phi(x) \int_x^{x+c} p H(t-x) dt = \phi(x), \quad (3.3) \end{aligned}$$

and this is a form of Fourier's theorem which Heaviside, using Taylor's theorem in the form

$$H(t-x) = e^{-xp} H(t),$$

expressed operationally as

$$\phi(x) = \int_{-w}^{+w} \phi(t) p e^{-xp} [1] dt. \quad (3.4)$$

He omitted the $[1]$ since "a unit operand is always understood, meaning the function whose value is $+1$ for $+$ values only of the variable."

Now, if we confine ourselves to values of t such that $c < t < w$, the factor $t^c/c!$ in our definition (2) of $H(t)$ becomes unity, and can be omitted. We thus have

$$\begin{aligned} p e^{-xp} [1] &= e^{-xp} p \left[\frac{1}{2} + \frac{1}{\pi} \text{Si}(nct) \right] \\ &= \frac{1}{\pi} e^{-xp} \frac{\sin(nct)}{t} = \frac{1}{\pi} e^{-xp} \int_0^{nc} \cos \lambda t d\lambda \\ &= \frac{1}{\pi} \int_0^{nc} \cos \lambda (t-x) d\lambda; \quad (3.5) \end{aligned}$$

so that, if we substitute this value in the above integral, we get Fourier's theorem in one of its usual forms.

Heaviside did not formulate $H(t)$, and thus did not proceed as above, but he reached the same result in other ways.

Impulse functions are used throughout Heaviside's book on Electromagnetic Theory. In an important section of vol. iii. pp. 234-291, entitled "The Solution of Definite Integrals by Differential Transformation," impulsive quantities are used in a collection of sixty-six striking examples, "beginning with easy ones." The first of these takes up less than a single page (236), most of which deals with preliminaries common to all the following cases. Heaviside then demonstrates three integral theorems. To each demonstration he gives one line, no more. The first two of these are well-known forms of Fourier's theorem. The third is another case of it, but it is also what is now known as Carson's integral equation, and is given in the precise form as afterwards stated by Carson*.

On p. 237 he deals with "Euler's most valuable fundamental integral, which is always turning up." He shows "its impulsive meaning," and says "of all definite integrals I admire it the most, because of its leading to so many others so easily." He adds, significantly, "but it must usually be interpreted in accordance with the impulsive integral. . . to show its power." On p. 238, with the aid of two impulse functions involving independent variables, t and x , he gives (in the course of four lines) a demonstration of "the Bessel expansion theorem for the zeroth function. It comes out in a singularly simple manner."

Now no one will claim that these demonstrations are firm proofs as they stand, yet I think it must be admitted that, with a slight change of wording, they can be made such, provided that we can assume the properties of $H(t)$. We shall see that in order to prove these properties it is merely necessary to put Fourier's theorem into a form suitable for infinitesimals. It will be noted that $H(t)$ involves the sine-integral function. It is by no means new to come across this function in connexion with Fourier's theorem, since many proofs of this theorem, if examined, will be found to involve the Si function either in some explicit or in some latent form. In Bertrand's 'Calcul Integral,' 1870, pp. 228-239, it will be found that Fourier's theorem

* 'Electric Circuit Theory and the Operational Calculus,' McGraw-Hill, New York, p. 19, equation 29. Carson states, "It is on this equation that we shall base our discussion of operational methods, and from which we shall derive the rules of the Operational Calculus."

is developed from properties of this function*. The truth of the matter appears to be that the sine-integral function is the root of the tree of which Fourier's theorem is the trunk and of which many important integral theorems are the branches.

4. THE WAVES OF $\text{Si}(nct)$ AND OF ITS DERIVATIVE.

One of the earliest uses Fourier made of his integral was to sum the series †

$$\sum_{s=0}^{\infty} \frac{\sin(2s+1)u}{2s+1}.$$

This led him to the $\text{Si}(x)$ function and to a proof that $\text{Si}(\infty) = \pi/2$ by making use of the fact that the sum of the series was known to be $\pi/4$. Let us use exactly the same process to find S_n , the sum of n terms of the series

$$S_n \equiv \frac{1}{\pi} \sum_{r=1}^n \sin r\theta \int_0^{\pi} \sin(r\phi) d\phi. \quad \dots (4)$$

S_n is a periodic function of θ with semiperiod π . If we make $\theta = \pi t/l = ct$ where c is an infinitesimal, the semi-wave-length will be l or π/c , a *fixed* infinity. Since the integral vanishes for even values of r , and becomes $2/r$ for odd values of r , every second term of the series becomes zero; but we can still look upon n as an odd integer denoting the number of terms. If we put $r = 2m+1$, where m is a positive integer, we have

$$S_n = \frac{2}{\pi} \sum_{m=1}^n \frac{\sin(2m+1)ct}{2m+1} = \frac{1}{\pi} \sum_{q=c}^{nc} \Delta q \frac{\sin qt}{q}, \quad (4.1)$$

where

$$q = (2m+1)c \quad \text{and} \quad \Delta q = 2c.$$

Now we are justified in replacing this by the Fourier integral

$$S_n = \frac{1}{\pi} \int_c^{nc} \frac{\sin qt}{q} dq$$

* If reference be made to Fourier's remarks on "the singular property" of certain impulsive quantities [*'Theory of Heat'* (Freeman), pp. 208 and 351], or to the properties of the first form of Dirichlet's integral as given in Carslaw's book (*'Fourier Series'*, p. 200 &c.), it will be seen that the early work leading up to Fourier's theorem came very close to recognizing the impulse function as conceived by Heaviside. Yet it did not quite do so. The aim of the present paper is to give precision to Heaviside's idea.

† Fourier's *'Theory of Heat'*, Freeman's translation, p. 346 (1878).

if, and only if, the increase in the argument qt for the *fixed* increment $\Delta q = 2c$ is negligible compared with 2π . This point is more fully dealt with in the Appendix. The increment of qt is $2ct$, and although c is infinitesimal, t may be so large as to overpower it. We assume that t is never greater numerically than a fixed quantity w , which, although possibly infinite, is such that cw is infinitesimal. We then have

$$\begin{aligned} S_n &= \frac{1}{\pi} \int_c^{nc} \frac{\sin qt}{q} dt = \frac{1}{\pi} \int_{ct}^{nct} \frac{\sin z}{z} dz \\ &= \frac{1}{\pi} [\text{Si}(nct) - \text{Si}(ct)]. \end{aligned} \quad (4.2)$$

The assumption made about w implies that w can never be comparable with the half wave-length π/c , since otherwise cw would be finite, or even infinite. We are thus dealing with values of t which, though possibly infinite compared with the unit, are also infinitesimal compared with the half wave-length of the periodic function S_n . We can make t as small as we like, but not greater than w .

The quantities n, c, w , referred to in the definition of $H(t)$, have not been chosen arbitrarily, since they have each a definite meaning in connexion with the Fourier series. The number of terms of the series is n , and this is an infinity without upper bound. We do not use ∞ for n , because n is definite and mathematical while ∞ is not so. The infinite wave-length of the periodic function is fixed by the infinitesimal c , while w is an infinite upper limit imposed upon t in order to make sure that the Fourier integral represents the sum of the series.

Let us now consider the function

$$H_{01}(t) \equiv \frac{1}{2} + \frac{1}{\pi} \text{Si}(nct). \quad . \quad . \quad . \quad (4.3)$$

For finite values of t , H_{01} is unity if t be positive and zero if t be negative, provided we neglect high infinitesimals. If we want to secure this result for all values of t ranging from c upwards we must make n such that nc^2 is infinite. Now, although n is without upper bound, if we make n indefinitely infinite we throw away precision and make it impossible to calculate H_{01} for infinitesimal values of t . Let m be a number such that

$$nc \cdot c^m = 1; \quad . \quad . \quad . \quad . \quad (4.4)$$

since n must be an integer, this equation defines a curious sequence for m . We contemplate making m an infinity of as high an order as, or of even higher order than, v^v where $v=1/c$; but for the present let us assume merely that m is positive and greater than unity. We then have

$$\text{Si}(nct) \equiv \text{Si}\left(\frac{t}{c^m}\right) \equiv \text{Si}(\xi),$$

where in the last expression we measure t in terms of a new unit c^m , and put $t=\xi c^m$, where ξ is the number of these new units denoting t . We also have

$$\begin{aligned} \text{Si}(\xi) &= \int_0^\xi \frac{\sin z}{z} dz = \xi - \frac{\xi^3}{3!3} + \frac{\xi^5}{5!5} \&c. \\ \frac{d \text{Si}(\xi)}{d\xi} &= \frac{\sin \xi}{\xi}, \text{ and } \frac{d \text{Si}(\xi)}{dt} = \frac{\sin \xi}{t}. \end{aligned} \quad (4.5)$$

The function $\text{Si}(\xi)$ has been long known, and tables of its calculated values have been published*.

Its properties, so far as needed for present purposes, can perhaps be most clearly seen from simple graphical considerations. The adjoining figure shows curves for $y=\sin \xi$, ($Q, Q_1, Q_2 \dots$), $\eta=\text{Si} \xi$, ($P, P_1, P_2 \dots$), and another curve u whose ordinates measure the slope of the curve η . The abscissæ represent ξ in units equal to π . If Q be any point on y , and P the corresponding point on η , the tangent to the curve η at P is parallel to OQ . If we produce OQ to R , a point on the ordinate P_1Q_1 at $\xi=\pi$, and if RU be a horizontal meeting PQ in U , the locus of U will be the curve u . The tangent to y and also to η at the origin is such that its ordinate at Q_1 is π . This value is the maximum ordinate of the curve u and occurs at $\xi=0$. The curve η can readily be drawn. Its slope at zero is greater than that at any other point, and as ξ increases this slope diminishes till η reaches its greatest maximum at P_1 , for which $\xi=\pi$. Maxima occur at $(2s+1)\pi$ and minima at $2s\pi$ for each positive integer s , and at these points y and u each pass through zero values. The tangents, drawn from O to the sine curve y touch this at points whose abscissæ give the turning point, of u and also the points of inflexion of η , while the intercepts of these tangents on any vertical such as Q_1P_1 , and measured from Q_1 , will be an accurate measure of the fluctuations of u about zero, and also after the first

* Brit. Assoc. Reports, pp. 248-251 (1927) and 316-318 (1928), where references are given to previous work by Lord Rayleigh, Proc. R. S. xi. p. 320 (1914), and also by Glaisher, Phil. Trans. clx. p. 367 (1870).

as *c*. This makes it simple to calculate the fluctuations of $\text{Si}(nct)$ by integrating

$$\frac{d}{dt} \text{Si}(nct) = \frac{\sin(nct)}{t}$$

over a few wave-lengths, since we can regard *t*, though not $\sin(nct)$, as constant throughout the integration. If we do so from some point near *t* up to *t* we get

$$\text{Si}(nct) = \kappa - \frac{\cos(nct)}{nct}, \quad (4.6)$$

where κ is some constant. Since the average value of $\text{Si}(nct)$ for a complete wave, with *t* finite, must be $+\pi/2$ if *t* is +, and $-\pi/2$ if *t* is -, we must put for κ one of these values according to the sign of *t*.

The fluctuation of $\text{Si}(nct)$ about this level value $\pm\pi/2$ must thus have

$$\left. \begin{array}{l} \text{amplitude} \quad \alpha = \frac{1}{nct} = \frac{c^m}{t}, \\ \text{wave-length} \quad = 2\pi/nc = 2\pi c^m. \end{array} \right\} (4.7)$$

The formula for the amplitude does not hold for highly infinitesimal values of *t*, but simple consideration of the curve shows that, even if *s* is not very large,

$$\alpha = \frac{1}{\pi(s - \frac{1}{4})},$$

where

$$\pi s = t/c^m,$$

is a good approximation to α , the divergence from the level value.

From the published data it is possible to deduce figures given in the table below referring to the first few waves, which are here of special interest. It will be seen that α soon approaches the value $1/\pi(s - \frac{1}{4})$. The table explains itself, except that the last column shows $\Delta \text{Si}(\xi)$, the fluctuation of $\text{Si}(\xi)$ between successive integral values of *s*. $\Delta \text{Si}(\xi)$ is the area of the corresponding half-wave of the derivative of $\text{Si}(\xi)$ represented by the curve *u*.

<i>s</i> .	ξ .	$\text{Si}(\xi)$.	$\pm \alpha$.	$\alpha\pi(s - \frac{1}{4})$.	$\pm \Delta \text{Si}(\xi)$.
1	π	1.8519	.2811	.66	1.8519
2	2π	1.4183	.1525	.90	.4336
3	3π	1.6147	.1039	.91	.2564
4	4π	1.4922	.0786	.92	.1825
5	5π	1.6339	.0632	.94	.1417
10	10π	1.5391	.0317	.97	—

Summarizing results, we have, for all values of $|t|$ between c and w ,

$$H_{01}(t) = [1] - \frac{\cos(nct)}{\pi nct}, \quad . \quad . \quad . \quad (4.8)$$

where $[1]$ is unity if t be $+ve$, and zero if t be $-ve$; but if t is of the order c^m , the fluctuations α are finite, about a level value unity if t be $+ve$ with greatest value $+0.2811/\pi$ at $t=\pi c^m$, and about a level value zero if t be $-ve$ with numerically greatest value $-0.2811/\pi$ at $t=-\pi c^m$.

The orders of magnitude of α , of the fluctuation of $Si(nct)$, or $\Delta Si(nct)$; and of u , the derivative $p.Si(nct)$, are as follows:—

	Order of Magnitude.					
Of t	c^m	c	finite	w	}	(4.9)
Of $\Delta Si(nct)$, or α ..	finite	c^{m-1}	c^m	c^m/w		
Of u , or $p.Si(nct)$...	$1/c^m$	$1/c$	finite	$1/w$		

Thus for finite values of t , or even when t is as small as c , the fluctuations α of $Si(nct)$ and of $H_{01}(t)$ are highly infinitesimal; but, in view of what follows, it should be noted that this is not at all the case with u , the derivative of $H_{01}(t)$, because u is finite for ordinary values of t , though it fluctuates about a zero value.

The amplitude of u becomes highly infinite as t verges on zero, and reference to the curve and table shows that the first positive pulse of u extends over two half-waves, one on each side of zero, and that its area is over eight times as great as that of the first negative pulse. By making m infinite we can crowd all the finite fluctuations of H_{01} into a range of order c^m on each side of zero, but the fluctuations * themselves remain unaltered in magnitude.

On reference to the definition of $H(t)$ and of its properties, given at (2), it will be seen that $H_{01}(t)$ has all the properties (2.1), (2.3), (2.4), and (2.5), but only some of the properties (2.2); since H_{01} , except for infinitesimals, is zero for all values of t between $-w$ and $-c$, but becomes finite when t is as small as a negative finite multiple of c^m .

For many purposes H_{01} will serve as Heaviside's unit function, but it is an important point in much of his analysis that $H(t)$ must be zero for all negative values of the variable up to and including zero absolute.

* These fluctuations represent "Gibbs' phenomenon" for the case $n=\infty$. See Carslaw's 'Fourier Series and Integrals,' chapter ix., particularly figs. 35 and 36, pp. 273, 274.

This result can be secured, except for high infinitesimals, by introducing the factor $\frac{t^c}{c!}$, as shown at (2).

5. THE FUNCTION $t^c/c!$.

The function $t^c/c!$, where c is a high infinitesimal, looks simple enough, but has many striking properties. We have, except for infinitesimals,

$$c! \equiv \Gamma(c+1) = 1,$$

$$\lambda^c = 1 \quad \text{if } \lambda \text{ be finite,}$$

$$c^c = 1 \quad \text{since } x^x \rightarrow 1 \quad \text{as } x \rightarrow 0.$$

The infinitesimals of $c!$ can be readily obtained from the known formula for $\log c!$; but those associated with λ^c , or c^c , appear to be unknown*.

It follows that the function $y = t^c/c!$ must be unity for all values of t represented by

$$\lambda_1 c^{\lambda_2}, \quad \lambda_1, \quad \text{or} \quad \lambda_1 \left(\frac{1}{c}\right)^{\lambda_2},$$

where λ_1 and λ_2 are any finite quantities.

This is not the case if we make λ_2 infinite. Thus, if we put $(1/c) \equiv v$, and

$$\left. \begin{array}{ll} \text{if} & t = c, c^v, c^{v^2}, \dots \\ \text{we have} & y = 1, c, c^v, \dots \\ \text{while if} & t = v, v^v, v^{v^2}, \dots \\ \text{we have} & y = 1, v, v^v, \dots \end{array} \right\} \dots \dots \dots (5.1)$$

In the former case we get high infinitesimals and in the latter high infinities. Moreover, if we define

$$y_1 \equiv t^{-c}/(-c)!,$$

we have

$$yy_1 = t^c t^{-c}/c! (-c)! = 1;$$

so that y_1 is the reciprocal of y , and becomes infinite as

* If the above equations could be regarded as identities, a simple integration will show that

$$u \equiv \frac{1}{2c^2} \left[\frac{t^c}{c!} - \frac{t^{-c}}{(-c)!} \right]$$

would have all the properties required in an impulse function, *i. e.*, that its integral from $-v$ to $+v$ is the same as that from $-c$ to $+c$ and is unity.

$t \rightarrow 0$, and infinitesimal as $t \rightarrow \infty$. Some curious results follow :—

If $f(t)$ be a function suspected of having a finite discontinuity at $t=a$,

$$f_1(t) \equiv f(t) \times \frac{(t-a)^c}{c!}$$

is a function exactly equal to $f(t)$ for all values of t except those within the range $(a-c)$ to $(a+c)$, while throughout this range it is perfectly continuous and becomes zero on each side of $t=a$.

The spot-function

$$f(t) \left[1 - \frac{(t-a)^c}{c!} - \frac{(t-b)^c}{c!} \right]$$

is zero for all values of t , except at $t=a$, when it becomes $f(a)$, and at $t=b$, when it becomes $f(b)$.

The function

$$f(t) \left[\frac{(t-a)^c}{c!} - \frac{(t-a)^{-c}}{(-c)!} \right]$$

is zero except at $t=a$, when it is infinite.

In all cases in which t is restricted to positive values the function $y = t^c/c!$ will serve as Heaviside's unit function, and its derivative $u \equiv p.y$ will be an impulse function*. In any physical example in which a constant force F is said to be "impressed" or "applied" at $t=0$, we have the case of an impulsive force which can be accurately formulated for all positive values of t by

$$F(t) = Fp \cdot \frac{t^c}{c!}$$

where F is the impulse of $F(t)$, since

$$\int_0^{\infty} F(t) dt = F \int_0^{\infty} p \cdot \frac{t^c}{c!} dt = F \int_0^c p \frac{t^c}{c!} dt = F. \quad (5.2)$$

* Reference should be made to 'Electromagnetic Theory,' ii. pp. 54-55 on the "Theory of an Impulsive Current," and pp. 63-65 on the "Nature and Effect of Multiple Impulses." Heaviside's argument becomes quite clear and precise if by $p.Q$ is understood $p.Q t^c/c!$, the impulse of which is its integral from $t=0$ to $t=\infty$, and is simply the (constant) quantity Q . Heaviside denotes impulse functions in several ways. Those based on Fourier's theorem are variants of $H_{01}(t)$. Others are denoted by $p.1$ or by $t^{-1}/(-1)!$. These expressions can be reconciled with each other, and also with the use of Heaviside's index operator, by simply introducing an infinitesimal c . Thus we can replace

$p.1$ by $p.p^{-c}.1$, $p t^c/c!$, $p^{1-c}.1$, or $t^{c-1}/(c-1)!$.

For present purposes our interest in this function is to consider its effect on $H(t)$ for negative values of t , where

$$H(t) = \frac{t^c}{c!} H_{01}(t).$$

When t is negative the greatest numerical value of $H_{01}(t)$ is $-0.2811/\pi$ or -0.0985 . This occurs at $-t = \pi c^m$, for which $te/c!$ becomes

$$\begin{aligned} &1 \text{ if } m \text{ is finite and } nc = v^m, \\ &c \text{ ,, } m \text{ ,, } v \text{ ,, } nc = v^v, \\ &c^v \text{ ,, } m \text{ ,, } v^2 \text{ ,, } nc = v^{v^2}. \end{aligned}$$

Thus by making the number of terms of the Fourier series sufficiently infinite, say v^{v^2} , we find that the value of $H(t)$, for negative value of t , is never greater numerically than $0.098 c^v$. For such a value of n the function $H(t)$ as defined at (2) is such that (i.) it has all the properties specified under 2.1 to 2.5, (ii.) for all ordinary values of t it becomes the same as $H_{01}(t)$, and (iii.) its infinitesimals are excessively minute both in amplitude and in wave-length, since these are each of the order c^{v^2} .

Now we have

$$H(t-x) = \frac{(t-x)^c}{c!} H_{01}(t-x),$$

and for ordinary values of t the only effect of $H_{01}(t-x)$ is to introduce a factor unity if $t > x$, and a factor zero if $t < x$. That is, if we are prepared to adopt as a convention that $(t-x)^c$ is zero whenever $t < x$, we can dispense with $H_{01}(t-x)$ altogether, and put

$$H(t-x) = \frac{(t-x)^c}{c!}.$$

This convention is not justifiable in itself because, although $(-1)^c$ has an infinite number of Demoivre values, it will be found that the infinitesimal c makes all these values coalesce into unity, so that we cannot consider any one of them to be zero. Yet, if the solution of our problem is represented by

$$\Delta H(t-x),$$

where Δ is some operation to be performed on $H(t-x)$, we can find

$$\Delta (t-x)^c/c!,$$

and separate this into two portions A and B, where A is the part for values of $t > x$, and B that for values of $t < x$. The $H_{01}(t-x)$ factor tells us that A is the solution required, and

that B has nothing to do with the problem. We get A directly if we adopt the convention stated, so that, provided we do so, we have for the impulse function

$$pe^{-xp} H(t) = p H(t-x) = pe^{-xp} \frac{t^c}{c!} = p^{1-c} e^{-xp} : 1,$$

and, except for the infinitesimal c , this is the form in which Heaviside expressed it operationally.

H consists of two factors, and it seems possible to use either factor alone if the influence of the other is kept in mind. We can also proceed in the manner of Heaviside, who omitted both factors, though he was the first to recognize H and its properties. The way of Heaviside has met with a disapproving silence, yet it has been used by everyone in the past without even recognizing H, and that too in the simplest physical problems.

Take the case of finding a current C, which is given as zero at the moment of closing, by means of a switch, a circuit in which C is governed by the differential equation

$$(R + Lp)C = E,$$

where, in usual units,

$$E = 10, R = 1, L = \cdot 01,$$

we get a formula stating that C reaches its steady value of 10 amperes in very much less time than a second. Everyone ignores the current of 2.7×10^{44} amperes given by the formula only one second previously. The switch was not then closed, but what has that to do with the mathematical problem? To formulate this problem in exact mathematical terms we must put for E, not 10, but $10H(t)$. In reaching the solution in the normal way all the properties of $H(t)$ are assumed, though $H(t)$ is not mentioned, and is not even recognized.

6. FOURIER'S THEOREM AS AN IMPULSE INTEGRAL.

The properties of the impulse function $u = p.H(t-x)$ are entirely due to the infinitesimals of $H(t)$. The most extraordinary of all these properties arises from the fact that the wave-length of these infinitesimals is so excessively minute. Fourier's theorem can be written

$$\begin{aligned} \phi(x) &= \int_{-w}^{+w} \phi(t) u \cdot dt = \int_x^{x+c} \phi(t) u \, dt \\ &= \phi(x) \int_x^{x+c} u \, dt = \phi(x). \quad . \quad . \quad . \quad . \quad (6) \end{aligned}$$

This in appearance merely reproduces (3.3), but the difference is that while we have assumed in each case the properties of $H(t)$, in the case of (3.3) we have ignored its infinitesimals, and have thus assumed u to be zero except for the impulse range for which t and x differ by less than c . If we take account of the infinitesimals, we see from (4.9) that u is not zero, or even infinitesimal. It is finite for finite values of $(t-x)$, and is infinite as soon as $(t-x)$ becomes an infinitesimal of order c . Now Fourier's double integral can be put into the form (6), so that it must be possible to prove that for *any* increment ∂t which does not include values of t within the range $x < t < x+c$

$$\int_t^{t+\partial t} \phi(t) u dt = 0, \quad . \quad . \quad . \quad . \quad (6.1)$$

since it is the very essence of Fourier's theorem that $\phi(x)$ can be quite arbitrary for every value of x between $\pm w$. The integral over the element ∂t must thus be quite independent of the integral over any other element, and must be zero if Fourier's theorem is to hold. This striking result must also be independent of the arbitrary function $\phi(t)$, and thus we must necessarily have

$$\int_t^{t+\partial t} u dt = 0, \quad . \quad . \quad . \quad . \quad (6.2)$$

for *any* element ∂t , not including a portion, or the whole of, the impulse element x to $x+c$. Judging from my own experience, this point will be found obscure until it is noticed that u is an alternating function of the time t , and one of excessively high frequency. The integral is like the reading of a direct current galvanometer used with an alternating current. The moving system remains at rest, not because the deflecting forces u acting upon it are zero, but because they are alternately positive and negative, and cancel each other. The result would be very different if the turning forces were a measure of the average value of u^2 , as in an alternate current instrument, or if the instrument responded to the (unlimited) "total fluctuation" of the quantity u . The factor $\phi(t)$, in the preceding integral, does not alter the nature of this result, it simply multiplies the amplitude of the alternating quantity. Even if $\phi(t)$ is infinite (in some definite way) it must still be the fact that the amplitude of $\phi \times u$ remains sensibly constant throughout many wave-lengths of u . The integral over the stretch ∂t cannot depend upon ∂t , but simply upon the excess of ∂t over

the nearest integral number of wave-lengths ($2\pi c^m$) whose sum is less than ∂t , and, in view of the value of c^m , this residue must be a very high infinitesimal. Nothing can alter this result unless $\phi(t)$ includes an alternating portion in resonance with the frequency of u , and this is a far-fetched assumption.

Thus, although u is not zero as is assumed in (3.1) and (3.2), we reach the required result in (6.1) and (6.2) after taking account of infinitesimals, and this is all that is needed to justify (6) and the corresponding conclusions reached in (3.4) and (3.5).

Heaviside recognized clearly the impulsive nature of the quantities used in Fourier's integral. The earlier chapters of vol. ii. of 'Electromagnetic Theory' give an illuminating account of Fourier's theorem from this point of view, and of its connexion with relationships derived by means of his operator methods. His position is well summarized in a passage* short enough to quote. He takes

$$u = \frac{2}{l} \sum_{s=1}^{\infty} \sin \frac{s\pi x}{l} \sin \frac{s\pi y}{l}, \quad . . . \quad (6.3)$$

and says " u represents 0 everywhere. . . except at the point $y=x$, where it is infinite. But its space total is 1. . . . The function u therefore expresses an impulsive function.

"If we multiply a continuous function of y , say $f(y)$, by u , an impulsive function which exists only at the point $y=x$, the product is obviously zero except at that point where it is infinite. But if we take the space total of the product $uf(y)$ the result is $f(x)$. For u only exists at x , and its total is 1. Thus

$$\int u f(y) dy = f(x)$$

if the limits include the point x . If not, the result is zero. This is the property made use of in Fourier and other series when employed to express arbitrary functions. The function u in the above or other special form spots a single value of the arbitrary function in virtue of its impulsiveness."

Now the wording used to describe impulsive quantities is in most cases loosely phrased, and Heaviside is as vague as, but not more so than, other writers. He is clearly thinking not of u , but of the impulse of u , the total amount of which is unity. Although he says that u "only exists at x ," and "represents 0 everywhere except at x ," he cannot mean that u , an explicit function both of x and of y , is zero for every

* Elec. Mag. Theory, ii, p. 93 (1899).

value of each of these quantities except when $x=y$. He neither gives nor refers to any proof of his statement, and seems to have used Fourier's theorem to convince himself that in essentials his statement must be true. No definition is given of "impulse" or "total impulse." The original notion of an impulsive quantity (see 1) as something which is zero everywhere except for a specified infinitesimal range of the variable over which its integral is finite, does not appear general enough to cover the impulsive quantities met with in Fourier's theorem. We need a wider definition of an impulse, and we can arrive at one from the idea that an impulse implies an integral, and that an integral is but a learned name for an average taken over the range of the integral. The following *definition* appears to meet the case, using c, w with the same meanings as hitherto.

Impulse and Total Impulse.

If u be a function of t , its impulse at t is

$$\int_t^{t+c} u \, dt,$$

and its total impulse is

$$\int_{-w}^{+w} u \, dt. \quad . \quad . \quad . \quad . \quad (6.5)$$

Impulse Function.

Let u be such that its *average* value for a range t to $t+c$ of its variable t is, for all values of t , an infinitesimal of order c^α where $\alpha > 1$, except for a special range $x < t < x+c$, for which the impulse of u is finite.

The quantity u is then an impulse function, and its total impulse is concentrated at x (6.6)

Now, excluding cases in which an entry is made into the special impulse range, the last definition means that

$$\frac{1}{c} \int_t^{t+c} u \, dt = \kappa c, \quad . \quad . \quad . \quad . \quad (6.7)$$

where κ is finite or infinitesimal, so that, if κ_m is the maximum value of κ for any range t_1 to t_2 , we have

$$\frac{1}{t_2 - t_1} \int_{t_1}^{t_2} u \, dt < \kappa_m c.$$

This holds even for the total range $2w$ from $-w$ to $+w$, if we exclude the impulse range, so that we have

$$\int_{-w}^{+w} u \, dt < \kappa_m c (2w - c). \quad . \quad . \quad . \quad . \quad (6.8)$$

This is infinitesimal, since κ_m is finite or infinitesimal, and the product cw is infinitesimal.

Now the above appears all that is necessary to justify the statement quoted from Heaviside's book provided that by u is meant the *average* of u over a range c of the variable, and provided also that it is possible to prove (6.7).

But in order to do this it is necessary to prove the basic part of Fourier's theorem by summing u as defined in (6.3) by means of a Fourier integral. The case is not identical with that treated in (4), but the result is of the same character, showing that u is an alternating function of the time whose frequency is measured by nc , where n is an unbounded infinity. The value of κ in (6.7) will be found to be very highly infinitesimal compared with c .

It thus appears that the $H(t)$ function is based throughout upon Fourier's theorem, and that, when the latter is expressed in impulsive form, what is done is not to establish a new theorem, but to vary the statement of an old one. Heaviside's work shows the analytical convenience which can often be secured by using the theorem in its impulsive form. A result of fundamental importance is that the Fourier double integral represents a perfectly continuous function of the variable. For let $\phi(x)$ be a quantity, however discontinuous, whose single real value can be determined for every value of x between two limits x_1 and x_2 . Fourier's integral determines a truly mathematical function $F(x)$ without a trace of discontinuity anywhere. $F(x)$ and $\phi(x)$ are functions which, though not identical, are numerically equivalent—that is to say, F and ϕ are such that the difference between them is infinitesimal compared with either, for every value of x between the limits stated. This result is secured by making the ordinate of F at x represent a special mean value of ϕ taken over an infinitesimal range c , such as to include the value x . This abolishes any discontinuity by welding the joint in ϕ so that F becomes continuous throughout.

In Fourier's proof of his theorem infinitesimals are not explicitly mentioned, yet at least one paragraph in his 'Theory of Heat'* shows that he was quite aware of their

* Freeman's translation, p. 199 (1878). It was not until the present paper was in the hands of the printers that I noticed in Fourier's book (pp. 425-432) three paragraphs (415-417) indicating a proof of his theorem based upon the impulse function. He states that this was given in his "earliest researches," so that presumably it is the original form of the theorem. It does not appear in the text-books, and it seems to have been forgotten, otherwise the fluctuations pointed out by Gibbs in 1899 could hardly have been regarded as a "phenomenon."

presence. We conclude by quoting this passage: "We must admit into analysis functions which have equal values, whenever the variable receives any values between two given limits, even though on substituting in these two functions, instead of the variable, a number included in another interval, the results of the two substitutions are not the same. The functions which enjoy this property are represented by different lines, which coincide in a definite portion only of their course, and offer a singular species of finite osculation." The word finite seems to refer to the limits, but the word osculation implies infinitesimal differences.

7. APPENDIX.—FOURIER'S THEOREM AND INFINITESIMALS.

Fourier, when proving his theorem, assumed the variable x to be finite. The application of his theorem to other values of x is quite simple, and merely needs reconsideration of the limits used in his integrals. For this purpose we take one of the cases dealt with in his 'Theory of Heat' (Freeman, 1878, p. 348), and restate his argument, after translating his notation to that of the present paper.

He takes

$$\frac{\pi}{2} \phi(u) = \sum_{r=1}^n \sin(ru) \int_0^{\pi} \phi(u) \sin(ru) du.$$

His argument involves three steps

- (i.) put $u = xc$, where c is an infinitesimal,
- (ii.) denote $\phi(u)$ or $\phi(xc)$, by $f(x)$,
- (iii.) let $q = rc$, so that $\Delta q = c$, since r alters by units.

Now if we define

$$F_s(x) \equiv \frac{2}{\pi} \sum_{r=1}^n \sin qx \int_0^{\pi} \phi(u) \sin(ru) du,$$

the theorem consists in expressing $F_s(x)$ as a double integral whose value is proved to be equal to $f(x)$ when n is made infinite.

Now on (i.), we have $\phi(u)$ is periodic, so that $F_s(x)$ must be so. The period of u is 2π , and that of x is $2\pi/c$. When we change the integral coefficient from an integral in u to one in x the limits of the new integral must be 0 and π/c , not 0 and ∞ ; because c , however infinitesimal it may be, must be regarded as a fixed quantity if there is to be any meaning at all in the periodicity of $F_s(x)$.

Next on (ii.), although $\phi(u)$ is changed to $f(x)$, the quantity c is not thereby suppressed. Each power of u in $\phi(u)$ is represented by the same power of xc in $f(x)$, even though the powers of c may be taken into the new coefficients of $f(x)$. All that has been done is to measure u in terms of a new unit, c , and x is the number of these new units representing u . This new unit must be considered fixed throughout analysis, since otherwise, instead of solving our problem, we are changing it as we proceed.

We thus have

$$F_s(x) \equiv \frac{2}{\pi} \sum_{r=1}^n \sin qx \int_0^{\frac{\pi}{c}} f(x) \sin (qx) c dx,$$

where $q=rc$, r is integral, c is fixed.

Now, however infinite we make n , we can still call it n , and regard it as a definite fixed integer. If, with Fourier, we convert to an integral by interpreting (iii.) as

$$c \equiv \Delta q = dq,$$

we get

$$F_s(x) = \frac{2}{\pi} \int_c^{nc} dq \sin qx \int_0^{\frac{\pi}{c}} f(x) \sin qx dx.$$

Fourier put $c=0$, $nc=\infty$, $\pi/c=\infty$, but the natural limits are as stated. The true limits are such that the ratio of the two infinities is infinite, as also the ratio of the two zeros. If the natural limits are retained it becomes possible to calculate $F_s(x)$ for infinitesimal values of x , while the integrations are even simpler than if the indefinite limits 0 and ∞ are substituted.

There are, moreover, limits to the range of x outside which the integral $F_s(x)$ cannot be relied upon to represent the series $F_s(x)$. These limits are $\pm w$, where w is an infinity, but one which is bounded. Going back to (iii.) we have $\Delta q=c$, which is a fixed infinitesimal, whereas dq in the integral is indefinitely infinitesimal.

Now

$$\int_0^{\frac{\pi}{c}} f(x) \sin (qx) dx = Q(q),$$

where $Q(q)$ is a function of q , not of x . Hence for the series we have

$$F_s(x) \equiv \frac{2}{\pi} \sum_{q=c}^{nc} \sin (qx) Q(q) \Delta q.$$

Since $\Delta q = c$, the corresponding increment of (qx) is (cx) . If x is finite or infinitesimal this increment is infinitesimal, so that $\sin(qx)$ does not appreciably alter till the change in q corresponds with an infinite number of elements each equal to c . Under these circumstances the integral $F_i(x)$ undoubtedly represents the series $F_s(x)$. But if x is infinite, unless the product xc is a very small number, which, strictly speaking, should be infinitesimal, the value of $\sin(qx) Q(q)$ will alter considerably, and may actually reverse, or at all events reach zero, more than once within the limits of a single element Δq of the integral. Under such conditions it is not safe to rely on the integral $F_i(x)$ to represent the series $F_s(x)$.

We thus reach limits $\pm w$ for x , where w is an infinity such that cw is infinitesimal.

Although it may not be certain that the integral represents the series for $x > w$, it may yet be the fact that it does so. I have found in one or two cases that the integral appears to hold up to the limits $\pm \pi/2c$, or to a quarter of the fundamental wave-length of the series, but not beyond such limits. The periodic property of the series is lost in the integral.

If now we define the integral as

$$F_i(x) \equiv \frac{2}{\pi} \int_c^{nc} dq \sin(qx) \int_0^w f(t) \sin(qt) dt,$$

we get

$$F_i(x) \equiv \frac{1}{\pi} \int_0^w f(t) u dt,$$

where

$$u = \int_c^{nc} [\cos q(t-x) - \cos q(t+x)] dq;$$

this yields four quantities, two of which vanish, and we have

$$u = u_1 - u_2,$$

where

$$u_1 = \frac{\sin nc(t-x)}{t-x} \quad \text{and} \quad u_2 = \frac{\sin nc(t+x)}{t+x}.$$

If reference be now made to (6), (6.1), and (6.2) it will be seen that, with t and x both positive, u_2 produces no effect upon the integral, which reduces to

$$F_i(x) = \frac{1}{\pi} \int_0^w f(t) u_1 dt,$$

and we have a case already considered.

It only remains to show what happens when $f(t)$ becomes discontinuous or infinite either outside or within the impulsive range

$$x-c < t < x+c.$$

Now, from (4.9) and (6.8) the integral of u_1 over any range, excluding the impulse range, is the corresponding alteration of the Si (net) function, and this is an infinitesimal of the order c^m . If therefore $1/c^z$ is the greatest value* of $f(t)$ for the range considered, we have, whether there are or are not discontinuities in $f(t)$,

$$\frac{1}{\pi} \int f(t) u_1 dt < c^{m-z}.$$

Now, even if z is an infinity as large as the most exacting critic cares to state, we are yet at liberty to put the lower bound of m such that $m=z^z$. The integral then can safely be neglected.

For the impulse range we have

$$\int_{x-c}^{x+c} u_1 dt = \pi,$$

and for this range, assuming no discontinuity in $f(t)$, we have $f(t)=f(x)$, so that

$$F_i(x) = \frac{1}{\pi} \int_{x-c}^{x+c} f(t) u_1 dt = f(x) \frac{1}{\pi} \int_{x-c}^{x+c} u_1 dt = f(x),$$

an equality, not an identity.

If there is a discontinuity at $t=\xi$ within the impulse range, and if

$$\frac{1}{\pi} \int_{x-c}^{\xi} u_1 dt = \lambda_1 \quad \text{and} \quad \frac{1}{\pi} \int_{\xi}^{x+c} u_1 dt = \lambda_2,$$

we have

$$\lambda_1 + \lambda_2 = 1,$$

and also

$$F_i(x) = \lambda_1 f(\xi-0) + \lambda_2 f(\xi+0).$$

If the discontinuity occurs when x and ξ are exactly equal, we have from symmetry

$$\lambda_1 = \lambda_2 = \frac{1}{2}.$$

So that

$$F_i(\xi) = \frac{1}{2} [f(\xi-0) + f(\xi+0)],$$

* We exclude any case in which $f(t)$ contains, as a factor, $1/(t-a)$, with t passing through a .

or Dirichlet's limit. But if x and ξ are not identical, and if we know their difference with sufficient precision—that is, within a negligible fraction of the wave-length $2\pi c^m$ where the lower bound of m is as stated above—nothing is easier than to calculate λ_1 and λ_2 , and thus $F_i(x)$. It will be seen that $F_i(x)$, as x increases through ξ , passes quite continuously from $f(\xi-0)$ to $f(\xi+0)$, since λ_1 changes from 1 to 0, and λ_2 from 0 to 1, in a perfectly continuous manner. The Fourier integral $F(x)$ is seen to be continuous however discontinuous $f(x)$ may be. F and f cannot therefore be identical. They are numerically equal in the sense that $F-f$ is infinitesimal compared with f , and that too for every value of x within the specified range of x . It is possible that many ordinary mathematical theorems state only numerical equalities in the above sense, because in the proof of such theorems it is usual to neglect an infinitesimal at some stage of the argument.

XXVII. On Simultaneous Operational Calculus.

By BALTH. VAN DER POL, D.Sc., and K. F. NIESSEN, D.Sc.*

1. ACCORDING to J. R. Carson † Heaviside's operational calculus can be based upon the transformation of a given function $h(x)$ into its "image" $f(p)$, related to the former one by means of

$$f(p) = p \int_0^{\infty} e^{-px} h(x) dx.$$

This relation between image and original we write

$$f(p) \doteq h(x).$$

If the image $f(p)$ is known, one can obtain the original function $h(x)$ in the way pointed out by Bromwich ‡, leading to one single function $h(x)$ only on account of a theorem of March ‡.

The number p , whose real part must be positive

$$\text{R}(p) > 0,$$

* Communicated by the Authors.

† J. R. Carson, 'Electric Circuit Theory and the Operational Calculus' (McGraw-Hill, New York, 1926).

‡ For references about these articles see Balth. van der Pol, *Phil. Mag.* viii. p. 861 (1929), which will be quoted as L. See also H. M. Macdonald, *Math. Soc. of London*, xxxv. p. 428 (1902).

is called the parameter which operationally belongs to x , although really $\frac{1}{p}$ (let p and x are related to one another as image and original :

$$\frac{1}{p} \doteq x.$$

We now wish to introduce a simultaneous operational calculus, where two variables x, y are treated operationally by means of two parameters p, q respectively.

$$\left. \begin{array}{l} \frac{1}{p} \doteq x, \\ \frac{1}{q} \doteq y, \end{array} \right\} \quad \text{or in general} \quad \left\{ \begin{array}{l} f_1(p) \doteq h_1(x), \\ f_2(q) \doteq h_2(y), \end{array} \right.$$

based upon

$$f_1(p) = p \int_0^{\infty} e^{-px} h_1(x) dx,$$

$$f_2(q) = q \int_0^{\infty} e^{-qy} h_2(y) dy.$$

As an example we will determine the original function $H(x, y)$ corresponding to the image:

$$\frac{1}{(p+q)^n} \doteq H(x, y).$$

Regarding for an instance q as a constant, we first investigate the interpretation $h(x)$ of

$$f_1(p) = \frac{1}{(p+q)^n} \doteq h_1(x).$$

Applying a known theorem (see Carson or van der Pol, l.c. (8)), we have

$$\frac{p}{p-c} f_1(p-c) \doteq e^{cx} h_1(x),$$

where c is any constant.

Choosing q for c , we get

$$\frac{p}{p-q} \cdot \frac{1}{p^n} \doteq e^{qx} h_1(x), \quad . \quad . \quad . \quad . \quad (1)$$

where the sign \doteq is related to the transformation $\frac{1}{p} \doteq x$.

We might better write

$$h_1(x) = h_q(x), \quad . \quad . \quad . \quad . \quad . \quad (2)$$

to indicate that there is still the parameter q left. Now we have, keeping q still constant,

$$\frac{p}{p-q} \doteq e^{qx}. \quad . \quad . \quad . \quad . \quad . \quad (3)$$

In the known theorem, that when

$$f(p) \doteq h(x),$$

it follows that

$$\frac{1}{p} f(p) \doteq \int_0^x h(x) dx, \quad . \quad . \quad . \quad . \quad . \quad (4)$$

it is tacitly understood that

$$\int_0^\infty h(x) dx < e^{p\infty}.$$

This is seen by performing the partial integration

$$\begin{aligned} p \int_0^\infty e^{-px} \int_0^x h(x) dx &= - \int_0^\infty \int_0^x h(x) dx d.e^{-px} \\ &= e^{-p\infty} \int_0^\infty h(x) dx + f(p)/p. \end{aligned}$$

Therefore the application of (4) to (3) is only permitted in the case

$$p > q,$$

giving

$$\frac{p}{p-q} \frac{1}{p^n} \doteq \int_0^x \dots \int_0^x e^{qx} (dx)^n.$$

This multiple integral can be transformed into a single one in a known way, so that

$$\frac{p}{p-q} \frac{1}{p^n} \doteq \int_0^x e^{q\xi} \frac{(x-\xi)^{n-1}}{(n-1)!} d\xi. \quad . \quad . \quad . \quad (5) *$$

* This transformation follows also directly when the left-hand side of (5) is written as

$$\frac{p}{p-q} \cdot \frac{1}{p^{n-1}} \cdot \frac{1}{p},$$

and is considered as a "produit de composition."

Comparing (5) and (1, 2) we find

$$e^{qx} h_q(x) = \int_0^x e^{q\xi} \frac{(x-\xi)^{n-1}}{(n-1)!} d\xi.$$

Writing $x - \xi = s,$

we obtain
$$h_q(x) = \frac{1}{(n-1)!} \int_0^x e^{-qs} s^{n-1} ds,$$

an incomplete gamma-function.

In order to find the required function $H(x, y)$ we have to transform $h_q(x)$ as a function of q operationally into a function of y :

$$f(q) = \frac{1}{(n-1)!} \int_0^x e^{-qs} s^{n-1} ds \doteq H(x, y). \quad . \quad . \quad (6)$$

With reference to I. form. (9) we have

$$e^{-sq} \doteq F_s(y) = \begin{cases} 0, & \text{for } y < s, \\ 1, & \text{for } y > s. \end{cases} \quad s > 0. \quad . \quad . \quad (7)$$

With the function $F_s(y)$, defined on the right-hand side of (7), we have from (6)

$$H(x, y) = \frac{1}{(n-1)!} \int_0^x F_s(y) s^{n-1} ds. \quad . \quad . \quad (8)$$

If we wish to know $H(x, y)$ for a set of variables x, y , where $x < y$, we have in $F_s(y)$ of (8) always $s < x < y$, and therefore from (7)

$$F_s(y) = 1 \quad \text{for } s < x < y,$$

so that

$$H(x, y) = \frac{1}{(n-1)!} \int_0^x s^{n-1} ds = \frac{x^n}{n!} \quad \text{for } x < y.$$

Seeking the value of $H(x, y)$ in the case $y < x$, we have

$$F_s(y) = 1 \quad \text{for } s < y,$$

$$F_s(y) = 0 \quad \text{for } y < s < x,$$

so that (6) becomes here

$$H(x, y) = \frac{1}{(n-1)!} \int_0^y s^{n-1} ds = \frac{y^n}{n!} \quad \text{for } y < x.$$

We can state the result in the following way:—

$$\frac{1}{(p+q)^n} \doteq H(x, y) = \begin{cases} \frac{x^n}{n!} & \text{for } x < y, \\ \frac{y^n}{n!} & \text{for } y < x. \end{cases} \quad . \quad . \quad (9)$$

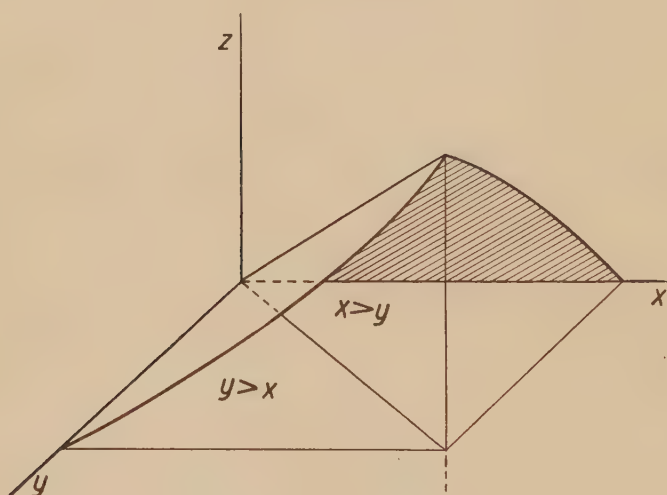
For $n=1$, $H(x, y)$ would become a kind of a "roof-function" when we measure $H(x, y)$ along the ordinate z above the region for positive values of x and y (see figure).

This geometrical interpretation is only given as an illustration, but will not be used more in what follows, where we wish again to draw attention entirely to the analytical side of the problem.

2. We will now consider an application of the simultaneous operational calculus to the evaluation of some integrals.

Suppose we require the value of

$$S = \int_0^\infty J_n^2(u) \frac{du}{u} \dots \dots \dots (10)$$



Writing

$$u = 2\sqrt{\xi}, \dots \dots \dots (11)$$

we wish to know

$$2S = \int_0^\infty J_n(2\sqrt{\xi}) J_n(2\sqrt{\xi}) \frac{1}{\xi} d\xi.$$

The reason for this substitution (11) is to bring the Bessel function and its argument in a form suitable for operational interpretation. In I. form. (29), namely, it is proved that when p and x belong together in

$$x = \frac{1}{p},$$

the following operational transformation exists :

$$x^{\frac{n}{2}} J_n(2\sqrt{x}) \doteq p^{-n} e^{-\frac{1}{p}}. \quad . \quad . \quad . \quad (12)$$

From the above it will be clear that we better write

$$2S = \int_0^\infty \frac{\xi^{\frac{n}{2}} J_n(2\sqrt{\xi}) \cdot \xi^{\frac{n}{2}} J_n(2\sqrt{\xi})}{\xi^{n+1}} d\xi.$$

Now for what follows the essential point is that we do not transform a function of ξ into a function of p , but that we first introduce new variables α and β , not instead of ξ , but entirely apart from ξ , namely, by constructing the function

$$S_{\alpha, \beta} = \int_0^\infty (\alpha \xi)^{\frac{n}{2}} J_n(2\sqrt{\alpha \xi}) \frac{(\beta \xi)^{\frac{n}{2}} J_n(2\sqrt{\beta \xi})}{\xi^{n+1}} d\xi. \quad (13)$$

For $\alpha = \beta = 1$ we have

$$S_{1,1} = 2S. \quad . \quad . \quad . \quad (14)$$

To evaluate $S_{\alpha, \beta}$ as a function of α and β we will use our operational methods :

a function of α will be transformed into a function of p ,

$$\alpha \doteq \frac{1}{p},$$

and a function of β into another of q ,

$$\beta \doteq \frac{1}{q}.$$

From the mentioned theorem (see (12), where p and x belong together) we know

$$\alpha^{\frac{n}{2}} J_n(2\sqrt{\alpha}) \doteq p^{-n} e^{-\frac{1}{p}}, \quad . \quad . \quad . \quad (15)$$

$$\beta^{\frac{n}{2}} J_n(2\sqrt{\beta}) \doteq q^{-n} e^{-\frac{1}{q}}. \quad . \quad . \quad . \quad (16)$$

In these operational relations ξ can be treated as a constant.

Now, using for an instance the notation of I. form. (5), it follows from

$$f(p) \doteq h(x)$$

that

$$f\left(\frac{p}{s}\right) \doteq h(sx),$$

if s is a positive number.

Applying this with $s=\xi$ and $x=\alpha$ or β , we find from (15, 16)

$$(\alpha\xi)^{\frac{n}{2}} J_n(2\sqrt{\alpha\xi}) \doteq \left(\frac{p}{\xi}\right)^{-n} e^{-\frac{\xi}{p}}, \quad . \quad . \quad (15a)$$

$$(\beta\xi)^{\frac{n}{2}} J_n(2\sqrt{\beta\xi}) \doteq \left(\frac{q}{\xi}\right)^{-n} e^{-\frac{\xi}{q}}. \quad . \quad . \quad (16a)$$

Therefore from (13)

$$\begin{aligned} S_{\alpha, \beta} &\doteq \int_0^\infty \frac{\left(\frac{p}{\xi}\right)^{-n} e^{-\frac{\xi}{p}} \left(\frac{q}{\xi}\right)^{-n} e^{-\frac{\xi}{q}}}{\xi^{n+1}} d\xi \\ &= \frac{1}{p^n q^n} \int_0^\infty e^{-\left(\frac{1}{p} + \frac{1}{q}\right)\xi} \xi^{n-1} d\xi. \end{aligned}$$

The symbol \doteq contains here the $\frac{1}{p} \doteq \alpha$ as well as the $\frac{1}{q} \doteq \beta$ transformation.

Substituting

$$\left(\frac{1}{p} + \frac{1}{q}\right)\xi = s,$$

we have

$$S_{\alpha, \beta} \doteq \frac{1}{(p+q)^n} \int_0^\infty e^{-s} s^{n-1} ds = \frac{\Pi(n-1)}{(p+q)^n}.$$

For the evaluation of $S_{\alpha, \beta}$ we need, therefore, the interpretation of $\frac{1}{(p+q)^n}$, which was found in the foregoing paragraph.

Applying (9), we obtain for $S_{\alpha, \beta}$

$$S_{\alpha, \beta} = \left\{ \begin{array}{ll} \frac{\Pi(n-1)}{\Pi(n)} \alpha^n, & \text{if } \alpha < \beta, \\ \frac{\Pi(n-1)}{\Pi(n)} \beta^n, & \text{if } \beta < \alpha, \end{array} \right\} . \quad . \quad (17)$$

and

$$S_{1,1} = \frac{1}{n}.$$

On account of (10) and (14) we find, therefore, for the required value of the integral S:

$$S = \int_0^\infty J_n^2(u) \frac{du}{u} = \frac{1}{2n}.$$

Meanwhile we found even more than that, since from (13) and (17) it follows that

$$\int_0^\infty \frac{J_n(2\sqrt{\alpha\xi})J_n(2\sqrt{\beta\xi})}{\xi} d\xi = \begin{cases} \frac{1}{n} \left(\frac{\alpha}{\beta}\right)^{\frac{n}{2}}, & \text{if } \alpha < \beta, \\ \frac{1}{n} \left(\frac{\beta}{\alpha}\right)^{\frac{n}{2}}, & \text{if } \beta < \alpha. \end{cases}$$

If we substitute

$$\xi = \frac{t^2}{4},$$

$$\alpha = a^2, \quad \beta = b^2,$$

we obtain a special case of the discontinuous integral of Weber and Schafheitlin (comp. Watson, 'Bessel Functions,' § 13, 42), namely

$$\int_0^\infty \frac{J_n(at)J_n(bt)}{t} dt = \begin{cases} \frac{1}{2n} \left(\frac{a}{b}\right)^n, & \text{if } a < b, \\ \frac{1}{2n} \left(\frac{b}{a}\right)^n, & \text{if } b < a. \end{cases}$$

3. Another application of simultaneous operational calculus can be made in the proof of the orthogonality relation for Bessel functions of the same order.

As is known, this relation is

$$\int_0^1 u J_n(au) J_n(bu) du = 0,$$

where a and b are two different roots of

$$J_n(x) = 0.$$

This has been found from the following equation:—

$$(a^2 - b^2) \int_0^1 u J_n(au) J_n(bu) du = a J_n(b) J_{n+1}(a) - b J_n(a) J_{n+1}(b). \quad (18)$$

This relation can be proved by operational methods as follows. Substituting

$$a = \sqrt{\alpha}, \quad b = \sqrt{\beta}, \quad u = 2\sqrt{\xi},$$

we have to prove

$$\begin{aligned} & (\alpha - \beta) \int_0^1 \frac{(\alpha\xi)^{\frac{n}{2}} J_n(2\sqrt{\alpha\xi}) (\beta\xi)^{\frac{n}{2}} J_n(2\sqrt{\beta\xi})}{\xi^n} d\xi \\ &= \frac{1}{2} \alpha^{\frac{n+1}{2}} J_{n+1}(\sqrt{\alpha}) \beta^{\frac{n}{2}} J_n(\sqrt{\beta}) - \frac{1}{2} \alpha^{\frac{n}{2}} J_n(\sqrt{\alpha}) \beta^{\frac{n+1}{2}} J_{n+1}(\sqrt{\beta}). \end{aligned} \quad (19)$$

If we relate

$$\alpha \doteq \frac{1}{p},$$

$$\beta \doteq \frac{1}{q},$$

and use again the equations (15a) and (16a), the right-hand side of (19) is transformed into

$$\frac{e^{-\frac{1}{4p} - \frac{1}{4q}}}{2^{2n+2} p^n q^n} \left(\frac{1}{p} - \frac{1}{q} \right) \dots \dots \dots (20)$$

For the transformation of the left-hand side of (19) we need the rule mentioned in I. form. (12), namely, it follows from

$$f(p) \doteq h(x),$$

that

$$\left(-p \frac{d}{dp} \right)^n f(p) \doteq x^n h(x), \quad n > 0.$$

This gives in our case ($n=1$, $x=\alpha$ or β):

$$\alpha (\alpha \xi)^{\frac{n}{2}} J_n(2\sqrt{\alpha \xi}) \doteq -p \frac{d}{dp} \left(\frac{\xi^n e^{-\frac{\xi}{p}}}{p^{n+1}} \right),$$

$$\beta (\beta \xi)^{\frac{n}{2}} J_n(2\sqrt{\beta \xi}) \doteq -q \frac{d}{dq} \left(\frac{\xi^n e^{-\frac{\xi}{q}}}{q^{n+1}} \right),$$

so that the left-hand side of (19) becomes

$$\frac{n+1}{p^n q^n} \left(\frac{1}{p} - \frac{1}{q} \right) \int_0^1 \xi^n e^{-\frac{\xi}{p} - \frac{\xi}{q}} d\xi - \frac{1}{p^n q^n} \left(\frac{1}{p^2} - \frac{1}{q^2} \right) \int_0^1 \xi^{n+1} e^{-\frac{\xi}{p} - \frac{\xi}{q}} d\xi. \dots \dots (21)$$

The equality between (20) and (21) is directly proved by introducing

$$s = \frac{1}{p} + \frac{1}{q},$$

and hence the required proof of (18) is given in an operational way.

Natuurkundig Laboratorium der
N. V. Philips' Gloeilampenfabrieken,
Eindhoven, July 1930.

XXVIII. *The Magneto-Optical Dispersion of Organic Liquids in the Ultra-violet Region of the Spectrum.*—Part II. *The Magneto-Optical Dispersion of Methyl Propionate, Ethyl Propionate, and Ethyl Formate.* By IDWAL JENKINS, B.Sc., and Prof. E. J. EVANS, D.Sc., Physics Department, University College of Swansea*.

THE apparatus and experimental methods employed in these investigations have been described in detail in Part I.†, and consequently only a brief reference to these points is necessary.

The light from a tungsten arc falls on a Bellingham-Stanley polarizing unit designed for work in the ultra-violet, and then traverses the liquid contained in a quartz polarimeter tube, which is placed symmetrically inside the core of a solenoid. The polarized beam, after emerging from the liquid, passes through the analyser and a quartz fluorite lens, which brings it to a focus on the slit of a quartz spectrograph. As the beam of light emerging from the polarizer consists of two semicircular fields with a horizontal line of demarcation, the vibrations in one half being polarized at a slight angle with those in the other, two spectra, one immediately above the other, are obtained at the camera end of the quartz spectrograph. The analyser is set at zero by adjusting its position so that these two spectra have the same intensity throughout their length when the magnetic field of the solenoid is not excited. There are four positions of the analyser for which this is possible, but one of the two positions of minimum intensity is chosen, as the instrument is then in its most sensitive position. The analyser is then rotated through an angle θ , and a photograph taken with the magnetic field excited. A second photograph was also taken on the same plate corresponding to a rotation θ on the opposite side of the zero with the magnetic field reversed. An examination of the photographic plate shows that there is a line of a definite wave-length, which has the same intensity in the upper and lower half of each spectrum. Let λ be the mean wave-length of this line as determined from the photograph, and θ_1 the rotation at this wave-length due to the quartz ends of the polarimeter tube. Then the value of Verdet's

* Communicated by the Authors.

† Stephens and Evans, *Phil. Mag.* x. p. 759 (1930).

constant δ of the liquid for wave-length λ is given by the equation

$$\theta_2 = \theta - \theta_1 = \delta \Sigma Hl,$$

where the summation is taken over the length of the liquid column. The current passing through the solenoid was kept constant at two amperes, and the magnetic field H at different points along the axis of the solenoid had been accurately measured. The value of ΣHl was 12270 cm. gauss.

The natural dispersion of the three liquids was determined in the visible spectrum by means of an accurate spectrometer, and in the region between $\cdot 51\mu$ and about $\cdot 27\mu$ photographically by means of the quartz spectrograph in which the Cornu prism had been replaced by a hollow glass prism with faces of optically worked fused quartz. Three slightly overlapping copper spectra were taken with the prism filled with the standard liquid, the liquid under investigation, and again with the standard liquid. In this way a slight shift of any part of the apparatus or a shift due to a change of temperature could be detected. The standard liquid employed was ethyl alcohol whose refractive indices at various wave-lengths had been accurately determined by Victor Henri*. The refractive index of the liquid under investigation at a definite wave-length can be determined by identifying a line of wave-length λ_1 due to refraction through the standard liquid, which coincides with a line of wave-length λ_2 due to refraction through the liquid under investigation. Then the refractive index of the liquid for a wave-length λ_2 equals the refractive index of the standard liquid for wave-length λ_1 .

The experimental results have been examined in relation to Larmor's† theory of magneto-optical rotation. According to this theory Verdet's constant δ is given by the expression

$$\delta = \frac{e}{2mC^2} \cdot \lambda \cdot \frac{dn}{d\lambda}, \quad (1)$$

where n is the refractive index, $\frac{e}{m}$ is the ratio of charge to mass of resonator, and C the velocity of light.

In the above expression the charge e is measured in electrostatic units and the magnetic field in electromagnetic units.

If the magneto-optical dispersion of a substance in the region of the spectrum investigated is controlled by one

* Victor Henri, 'Études de Photochimie,' p. 61.

† Larmor, 'Æther and Matter,' Appendix F.

EXPERIMENTAL RESULTS.

Natural Dispersion.

TABLE I. (a).

PHOTOGRAPHIC DETERMINATIONS.

19.2° C.		18.3° C.		12.8° C.	
Methyl Propionate.		Ethyl Propionate.		Ethyl Formate.	
Wave-length, λ , in microns.	Refractive index, n .	Wave-length, λ , in microns.	Refractive index, n .	Wave-length, λ , in microns.	Refractive index, n .
·5105	1.380 ₇	·5049	1.389 ₀	·5098	1.366 ₃
·4550	1.384 ₀	·4500	1.392 ₅	·4646	1.368 ₇
·4472	1.384 ₄	·4190	1.395 ₀	·4465	1.369 ₈
·4378	1.385 ₃	·4022	1.396 ₃	·4278	1.371 ₂
·4275	1.386 ₃	·3841	1.398 ₃	·4071	1.372 ₃
·4024	1.388 ₈	·3444	1.405 ₃	·3875	1.375 ₁
·3861	1.390 ₅	·3158	1.411 ₉	·3678	1.377 ₅
·3679	1.392 ₇	·3046	1.415 ₀	·3514	1.380
·3523	1.395 ₀	·2951	1.418 ₂	·3314	1.383 ₁
·3315	1.399 ₁			·3232	1.385 ₅
·3057	1.405 ₅			·3106	1.388 ₇
·2854	1.412 ₂			·3008	1.391 ₄
·2777	1.415 ₃			·2877	1.396 ₀
·2724	1.417 ₅			·2818	1.397 ₈
·2708	1.418 ₅			·2670	1.404 ₀

TABLE I. (b).

SPECTROMETER DETERMINATIONS AT THE ABOVE TEMPERATURES.

Wave-length, λ , in microns.	Refractive index, n .		
	Methyl Propionate.	Ethyl Propionate.	Ethyl Formate.
·6678	1.375 ₅	1.382 ₃	1.360 ₆
·5876	1.377 ₇	1.385 ₁	1.362 ₃
·5016	1.381 ₄	1.389 ₁	1.366 ₅
·4922	1.381 ₀	1.389 ₇	1.366 ₉
·4713	1.383 ₃	1.391 ₀	1.368 ₂
·4472	1.384 ₅	1.392 ₇	1.369 ₃

absorption band in the ultra-violet, and the natural dispersion is given by an equation of the Ketteler-Helmholtz type, it can be shown that

$$\phi = n\delta\lambda^2 = K_1 \left(\frac{\lambda^2}{\lambda^2 - \lambda_1^2} \right)^2, \quad \dots \quad (2)$$

where n and δ are the refractive index and Verdet's constant

for wave-length λ , K_1 a constant, and λ_1 the wave-length of the absorption band in the ultra-violet.

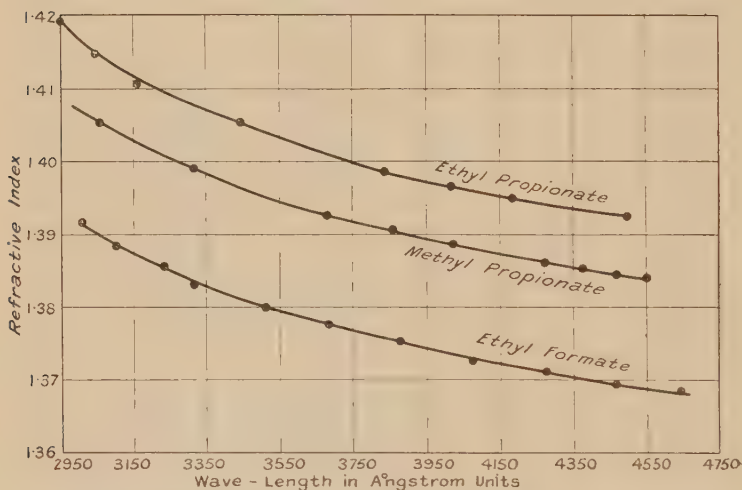
As will be seen later, the experimental results obtained in the present investigation can be represented by equation (2).

Magnetic Rotary Dispersion.

Methyl Propionate.

The methyl propionate used in the present investigation was the purest obtainable from Dr. Schuchardt Görlitz. In order that the purest possible specimens should be used the substance was subjected to a series of fractional distillations,

Fig. 1.



and the liquid which came over at exactly the correct boiling-point (79.9°C.) was used in the experiments.

The value of Verdet's constants for methyl propionate have been determined from $.4455\mu$ to $.3060\mu$. Experiments were conducted on two separate samples of the liquid, and the results are collected in Tables II. (a) and II (b).

Calculation of Constants.

In order to calculate the constants of equation (2) it is first necessary to obtain the values of the refractive indices *

* Although the refractive indices have not been determined at the same temperature as Verdet's constants, the values of λ_1 and K_1 will not be materially affected, as only the ratios enter into the calculations. Furthermore, the temperature correction only alters the refractive indices by about 1 in the third place of decimals.

corresponding to those wave-lengths for which Verdet's constants have been determined. The values of the refractive

TABLE II. (a).

Specimen I. of Methyl Propionate.

Temperature in °C.	Wave-length, λ , in microns.	Verdet's constant, \hat{c} , in min./cm. gauss.	Temperature in °C.	Wave-length, λ , in microns.	Verdet's constant, \hat{c} , in min./cm. gauss.
18.0	·4450	·0195 ₄	18.1	·3472	·0344 ₉
19.2	·4345	·0204 ₉	18.0	·3448	·0350 ₅
18.0	·4335	·0208	18.0	·3437	·0352 ₁
18.0	·4200	·0222	18.0	·3427	·0356 ₁
18.2	·4076	·0237 ₇	17.9	·3404	·0361
18.0	·3785	·0281 ₈	18.0	·3384	·0366 ₆
18.0	·3696	·0297 ₇	17.9	·3345	·0377
18.1	·3576	·0321 ₃	17.9	·3324	·0382 ₈
19.6	·3572	·0321	18.2	·3263	·0399
18.2	·3550	·0327 ₄	19.5	·3153	·0431 ₆
17.9	·3534	·0330 ₅	19.5	·3084	·0456
18.0	·3510	·0336 ₂	19.5	·3060	·0465 ₇
18.1	·3482	·0341 ₅			

TABLE II. (b).

Specimen II. of Methyl Propionate.

Temperature in °C.	Wave-length, λ , in microns.	Verdet's constant, \hat{c} , in min./cm. gauss.	Temperature in °C.	Wave-length, λ , in microns.	Verdet's constant, \hat{c} , in min./cm. gauss.
17.0	·4455	·0195 ₄	17.0	·3698	·0297 ₇
17.1	·4360	·0204 ₉	17.0	·3693	·0298 ₅
17.1	·4335	·0208	17.1	·3675	·0301 ₇
17.1	·4286	·0212 ₉	17.1	·3654	·0305 ₃
17.1	·4260	·0216	17.1	·3635	·0309 ₃
17.1	·4207	·0222	17.1	·3617	·0313 ₇
17.1	·4079	·0237 ₇	17.1	·3613	·0314 ₈
17.1	·3995	·0249 ₅	17.0	·3294	·0392 ₂
17.2	·3936	·0257 ₅	17.0	·3215	·0416 ₂
17.1	·3889	·0265 ₅	18.0	·3184	·0424 ₁
17.1	·3790	·0281 ₆	17.0	·3141	·0440 ₁
17.0	·3714	·0294 ₅	18.0	·3136	·0440 ₁

indices are read off fig. 1, and are given in Table II. (c), together with the corresponding values of Verdet's constant and wave-length.

Table II. (d) gives the values of λ_1 , the wave-length of the absorption band for methyl propionate, and of the constant K_1 obtained by solving equation (2). The values of λ_1 agree

Fig. 2.

Methyl Propionate.

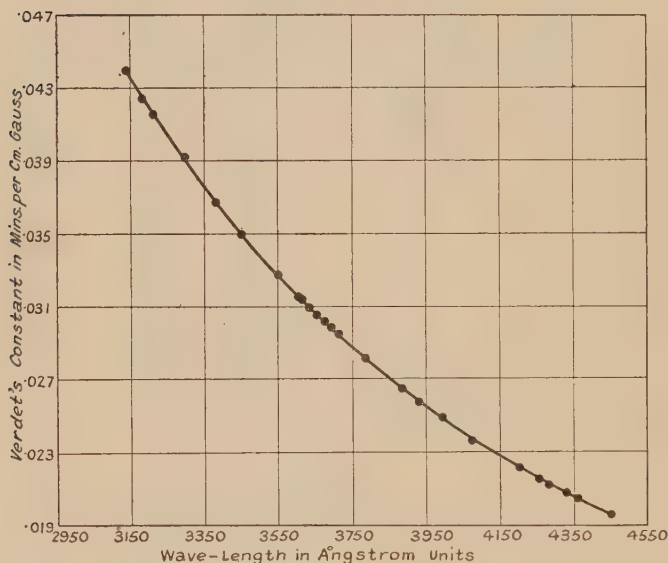


TABLE II. (c).

Methyl Propionate.

	Wave-length, λ , in microns.	Refractive index, n .	Verdet's constant, δ , in min./cm. gauss.
(a)	4360	1.385 ₅	0.0204 ₀
(b)	4207	1.386 ₉	0.0222
(c)	3995	1.389	0.0249 ₅
(d)	3790	1.391 ₂	0.0281 ₆
(e)	3613	1.393 ₇	0.0314 ₆
(f)	3294	1.399 ₆	0.0392 ₂
(g)	3141	1.403 ₂	0.0440 ₁

with one another within the experimental error, so that only one absorption band affects the rotation in the region of the spectrum investigated, and the experimental results are satisfactorily represented by equation (2).

TABLE II. (d).
Methyl Propionate.

From equations.	λ_1 in microns.	K_1 .
(a) and (d)	·1070	$4\cdot766_6 \times 10^{-3}$
(a) and (g)	·1065	$4\cdot771_4 \times 10^{-3}$
(b) and (e)	·1063	$4\cdot776_3 \times 10^{-3}$
(c) and (f)	·1069	$4\cdot767 \times 10^{-3}$
(d) and (g)	·1063	$4\cdot776_3 \times 10^{-3}$
(e) and (g)	·1065	$4\cdot771_4 \times 10^{-3}$

The mean values of λ_1 and K_1 from the above table are $\cdot1066\mu$ and $4\cdot771_5 \times 10^{-3}$ respectively.

The final equation for this liquid is therefore

$$n\delta = 4\cdot771_5 \times 10^{-3} \cdot \frac{\lambda^2}{\{\lambda^2 - (\cdot1066)^2\}^2} \cdot \cdot \cdot \quad (A)$$

In Table II. (e) a comparison is given between the values of Verdet's constants as determined experimentally at 17°C . and $17\cdot1^\circ\text{C}$. and those calculated for $17\cdot1^\circ\text{C}$. from the above formula.

TABLE II. (e).
Methyl Propionate.

Wave-length, λ .	δ (calculated).	δ (observed).
·4455	·0195 ₃	·0195 ₄
·4335	·0207 ₆	·0208
·3889	·0265 ₃	·0265 ₅
·3215	·0416 ₀	·0416 ₂

For sodium light ($\cdot5893\mu$) the refractive index of methyl propionate is $1\cdot377_7$, and the value calculated for Verdet's constant from the above equation is $\cdot0106_6$ at $17\cdot1^\circ\text{C}$. As far as the present authors are aware, the value of Verdet's constant of methyl propionate for sodium light has not been determined.

Variation of Verdet's Constant with Temperature.

The tables show that the temperatures of the determinations of Verdet's constant for the second specimen of methyl propionate were in nearly all cases $17\cdot0^\circ\text{C}$. or $17\cdot1^\circ\text{C}$., while for the first specimen the temperature varied between $17\cdot9^\circ\text{C}$. and $19\cdot6^\circ\text{C}$. The values of Verdet's constants at $17\cdot1^\circ\text{C}$. for wave-lengths given in Table II. (a) have been calculated from equation (A), and compared with the values

determined experimentally at different temperatures. From this comparison it is estimated that for methyl propionate Verdet's constant diminishes by about 0·3 per cent. per degree rise of temperature.

TABLE III. (a).
Specimen I. of Ethyl Propionate.

Temperature in °C.	Wave-length, λ , in microns.	Verdet's constant, δ , in min./cm. gauss.	Temperature in °C.	Wave-length, λ , in microns.	Verdet's constant, δ , in min./cm. gauss.
15·8	·4513	·0200 ₂	15·8	·3736	·0307 ₁
15·8	·4445	·0208 ₄	15·8	·3657	·0323 ₂
15·8	·4379	·0214 ₆	15·8	·3580	·0339 ₃
15·9	·4362	·0216 ₂	15·7	·3515	·0355 ₃
16·0	·4350	·0217 ₇	15·8	·3415	·0379 ₂
15·8	·4231	·0230 ₆	15·8	·3332	·0403 ₂
16·0	·4208	·0233 ₆	15·8	·3287	·0416 ₅
15·8	·4117	·0246 ₆	15·8	·3260	·0425 ₄
15·8	·4096	·0249 ₃	16·5	·3237	·0432 ₃
15·8	·4000	·0262 ₆	15·8	·3231	·0435 ₄
15·8	·3925	·0275 ₁	15·8	·3188	·0448 ₅
15·8	·3900	·0278 ₈	15·8	·3144	·0464 ₆
15·8	·3826	·0291	15·8	·3105	·0480 ₄

TABLE III. (b).
Specimen II. of Ethyl Propionate.

Temperature in °C.	Wave-length, λ , in microns.	Verdet's constant, δ , in min./cm. gauss.	Temperature in °C.	Wave-length, λ , in microns.	Verdet's constant, δ , in min./cm. gauss.
15·0	·4520	·0200 ₂	16·0	·3410	·0376 ₅
15·7	·4365	·0216 ₂	16·0	·3362	·0392 ₅
16·0	·4225	·0232 ₁	16·0	·3314	·0408 ₆
16·0	·3986	·0264 ₄	16·0	·3262	·0424 ₆
14·4	·3920	·0275 ₄	16·0	·3214	·0440 ₆
16·0	·3890	·0280 ₂	15·6	·3182	·0451 ₇
14·4	·3828	·0291 ₅	15·6	·3126	·0472 ₃
16·0	·3755	·0304 ₅	15·6	·3081	·0488 ₆
16·0	·3717	·0312 ₃	15·6	·3042	·0504 ₃
16·0	·3562	·0344 ₅	15·6	·3004	·0520 ₉
15·8	·3492	·0360 ₅			

Ethyl Propionate.

The ethyl propionate, which was obtained from Dr. Schuchardt Görlitz, was subjected to a process of fractional

distillation, and the fraction that came over at the correct boiling-point ($99.1^{\circ}\text{C}.$) was retained for measuring the magneto-optical rotation. The values of Verdet's constants

Fig. 3.
Ethyl Propionate.

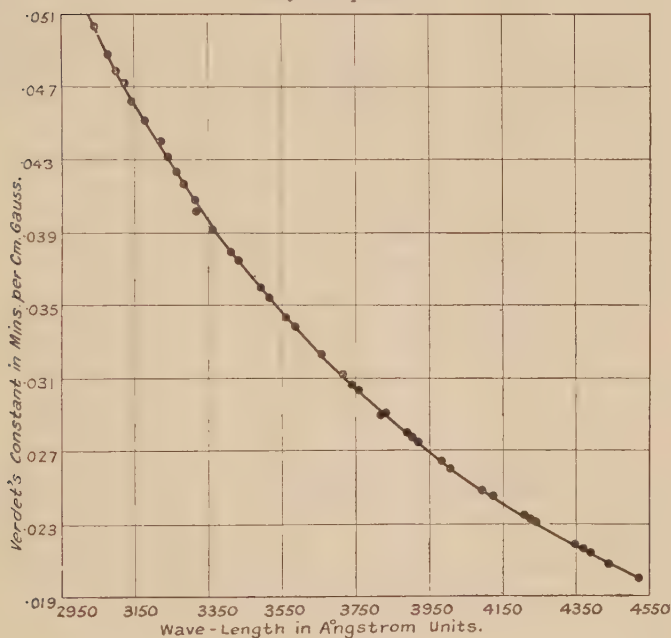


TABLE III. (c).
Ethyl Propionate.

	Wave-length, λ , in microns.	Refractive index, n .	Verdet's constant, δ , in min./cm. gauss.
(a)	4379	1.393 ₄	0.0214 ₆
(b)	4117	1.395 ₃	0.0246 ₆
(c)	3900	1.398 ₂	0.0278 ₆
(d)	3828	1.3990 ₅	0.0291 ₅
(e)	3515	1.404 ₂	0.0355 ₈
(f)	3314	1.407 ₇	0.0408 ₆
(g)	3004	1.416 ₄	0.0520 ₉

over the range of wave-length 4.5μ to 3.0μ were calculated from experiments on two separate samples of the distilled liquid, and the results are collected in Tables III. (a) and III. (b).

Calculation of Constants.

Table III. (c) gives the values of the refractive indices read off fig. 1 corresponding to the wave-lengths for which Verdet's constants have been determined.

As in the case of methyl propionate, it was found that equation (2) again represented the experimental facts, since all the values of λ_1 , the wave-length of the absorption band for ethyl propionate, agreed with one another within the experimental error. The values of λ_1 and K_1 are collected together in Table III. (d) below.

TABLE III. (d).
Ethyl Propionate.

From equations.	λ_1 in microns.	K_1 .
(a) and (d)	·1092	$5\cdot043 \times 10^{-3}$
(a) and (f)	·1070	$5\cdot070 \times 10^{-3}$
(b) and (e)	·1086	$5\cdot050 \times 10^{-3}$
(c) and (f)	·1073	$5\cdot063 \times 10^{-3}$
(d) and (g)	·1067	$5\cdot083 \times 10^{-3}$
(e) and (g)	·1062	$5\cdot096 \times 10^{-3}$

From the above table the mean value of λ_1 , the absorption band of ethyl propionate, is $\cdot1075\mu$ and the mean value of K_1 is $5\cdot068 \times 10^{-3}$.

TABLE III. (e).
Ethyl Propionate.

Wave-length, λ , in microns.	δ (calculated).	δ (observed).
·4513	·0200 ₉	·0200 ₂
·4225	·0232 ₇	·0232 ₁
·4000	·0262 ₈	·0262 ₆
·3717	·0311 ₉	·0312 ₃
·3430	·0377	·0376 ₅
·3188	·0450 ₂	·0448 ₅

The final equation for this liquid is therefore

$$n\delta = 5\cdot068 \times 10^{-3} \frac{\lambda^2}{\{\lambda^2 - (\cdot1075)^2\}^2} \dots \dots \dots (B).$$

In Table III. (e) above a comparison is given between the values of Verdet's constants as determined experimentally and those calculated from the above equation (B).

The value of Verdet's constant at the wave-length of sodium light ($\lambda = 5893$ and $n = 1.385$) derived from the present work is $\cdot 0112_7$ at 15.8°C .

Perkin * gives the specific rotation of ethyl propionate at 15.7°C . as $\cdot 8612$, and taking Verdet's constant for water as $\cdot 0131$, Perkin's results would give Verdet's constant for ethyl propionate as $\cdot 0112_8$.

TABLE IV. (a).

Ethyl Formate.

Temperature in $^\circ \text{C}$.	Wave-length, λ , in microns.	Verdet's constant, δ , in min./cm. gauss.	Temperature in $^\circ \text{C}$.	Wave-length, λ , in microns.	Verdet's constant, δ , in min./cm. gauss.
14.9	$\cdot 4489$	$\cdot 0192_1$	15.0	$\cdot 3512$	$\cdot 0336_1$
16.0	$\cdot 4402$	$\cdot 0200_0$	15.0	$\cdot 3412$	$\cdot 0360_2$
15.8	$\cdot 4330$	$\cdot 0208_0$	15.2	$\cdot 3320$	$\cdot 0384_2$
15.3	$\cdot 4259$	$\cdot 0216_1$	14.8	$\cdot 3236$	$\cdot 0408_2$
15.0	$\cdot 4063$	$\cdot 0240_1$	15.0	$\cdot 3164$	$\cdot 0432_2$
15.3	$\cdot 2905$	$\cdot 0264_1$	15.5	$\cdot 3095$	$\cdot 0456_2$
15.3	$\cdot 3750$	$\cdot 0288_2$	15.5	$\cdot 3034$	$\cdot 0480_3$
15.0	$\cdot 3622$	$\cdot 0312_2$			

TABLE IV. (b).

Ethyl Formate (after redistillation).

Temperature in $^\circ \text{C}$.	Wave-length, λ , in microns.	Verdet's constant, δ , in min./cm. gauss.	Temperature in $^\circ \text{C}$.	Wave-length, λ , in microns.	Verdet's constant, δ , in min./cm. gauss.
14.9	$\cdot 4491$	$\cdot 0192_1$	14.8	$\cdot 3411$	$\cdot 0360_2$
14.9	$\cdot 4258$	$\cdot 0216_1$	15.0	$\cdot 3318$	$\cdot 0384_2$
14.8	$\cdot 4064$	$\cdot 0240_1$	14.8	$\cdot 3236$	$\cdot 0408_2$
15.0	$\cdot 3905$	$\cdot 0264_1$	14.8	$\cdot 3165$	$\cdot 0432_2$
15.0	$\cdot 3750$	$\cdot 0288_2$	14.8	$\cdot 3096$	$\cdot 0456_2$
14.8	$\cdot 3623$	$\cdot 0312_2$	14.8	$\cdot 2973$	$\cdot 0504_2$
14.9	$\cdot 3512$	$\cdot 0336_1$			

Ethyl Formate.

The ethyl formate, which was also obtained from Dr. Schuchardt, was subjected to fractional distillation, and the fraction which came over at the correct boiling-point (54.3°C .) retained for the magnetic rotation experiments. The values of Verdet's constant for several wave-lengths between $\cdot 4489\mu$ to $\cdot 3034\mu$ were then measured. This sample of ethyl formate was again subjected to fractional distillation, and

* Journ. Chem. Soc. xlv. p. 496 (1884).

the liquid finally obtained was employed for determinations of the magnetic rotations at different wave-lengths. Although the values of Verdet's constant at given wave-lengths were

Fig. 4.

Ethyl Formate.

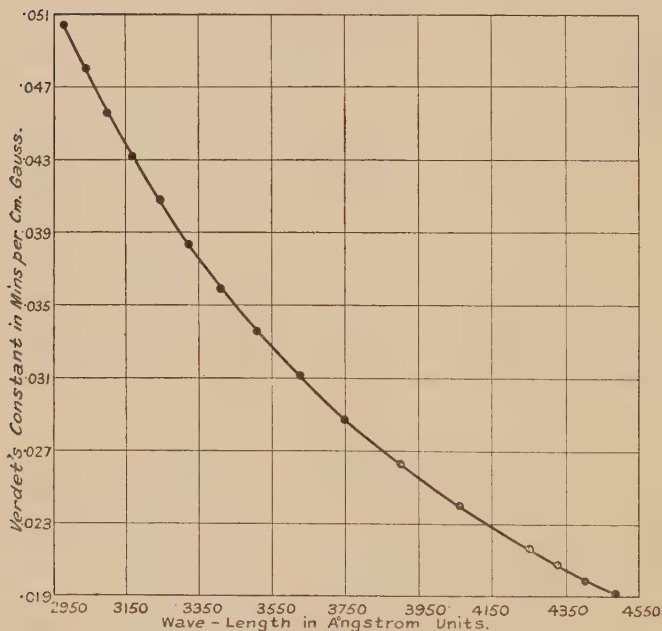


TABLE IV. (c).

Ethyl Formate.

	Wave-length, λ , in microns.	Refractive index, n .	Verdet's constant, δ , in min./cm. gauss.
(a)	4490	1.369 ₇	0.0192 ₁
(b)	4063	1.373 ₀	0.0240 ₁
(c)	3512	1.380 ₀	0.0336 ₁
(d)	3165	1.387 ₃	0.0432 ₂
(e)	2973	1.392 ₆	0.0504 ₂

found to be the same as those previously obtained, it was found possible to push the investigation a little further (2973 μ) into the ultra-violet region of the spectrum. The experimental results are given in Tables IV. (a) and IV. (b).

Calculation of Constants.

Table IV. (c) gives the values of the refractive indices read off fig. 1 corresponding to the wave-lengths for which the values of Verdet's constant have been determined.

As in the case of the previous two liquids, it is found that the magneto-optical effect in the region of the spectrum investigated can be considered as due to one absorption band of wave-length λ_1 , since the values of λ_1 , obtained by solving equation (2), agree within experimental error.

Table IV. (d) below gives the values of λ_1 and K_1 obtained from the solution of equation (2).

TABLE IV. (d).

Ethyl Formate.

From equations.	λ_1 in microns.	K_1 .
(a) and (b)	·1047	$4\cdot743 \times 10^{-3}$
(b) and (c)	·1059	$4\cdot727 \times 10^{-3}$
(c) and (d)	·1078	$4\cdot694 \times 10^{-3}$
(c) and (e)	·1062	$4\cdot722 \times 10^{-3}$
(a) and (d)	·1065	$4\cdot723 \times 10^{-3}$
(a) and (e)	·1054	$4\cdot731 \times 10^{-3}$

From the above table the mean value of λ_1 , the absorption band of ethyl formate, is $\cdot1061\mu$ and the mean value of K_1 is $4\cdot72 \times 10^{-3}$.

TABLE IV. (e).

Ethyl Formate.

Wave-length, λ , in microns.	δ (calculated).	δ (observed).
·4402	·0200 ₄	·0200 ₀
·3905	·0263 ₇	·0264 ₁
·3750	·0288 ₁	·0288 ₂
·3412	·0359 ₆	·0360 ₁
·3236	·0408 ₃	·0408 ₂
·3096	·0455 ₂	·0456 ₂

The final equation for this liquid therefore is

$$n\delta = 4\cdot72 \times 10^{-3} \frac{\lambda^2}{\{\lambda^2 - (\cdot1061)^2\}^2} \cdot \cdot \cdot \quad (C)$$

Table IV. (e) above gives a comparison between the values of Verdet's constants as determined experimentally and those calculated from the above formula (C).

The value of Verdet's constant at the wave-length of sodium light (5893μ and $n=1.362_7$) derived from the present work is $.0106_5$ at 14.8°C .

Perkin* gives the specific rotation for ethyl formate at 16.5°C . as $.8078$, and it is estimated from his results that the diminution in specific rotation per degree rise in temperature is 0.3 per cent. The specific rotation at 14.8°C . is therefore $.812$. Taking Verdet's constant for water as $.0131$, Perkin's results would give Verdet's constant for ethyl formate as $.0106_4$ at 14.8°C .

THE VALUE OF $\frac{e}{m}$.

The magnetic rotary power δ of any substance has been shown by Larmor† to be given by the equation

$$\delta = \frac{e}{2mc^2} \lambda \frac{dn}{d\lambda}, \quad \dots \dots \dots (1)$$

where c = vel. of light, $\frac{e}{m}$ = ratio of the charge to the mass

when e is measured in e.s.u., λ = wave-length measured in cm., and δ = Verdet's constant in radians/cm. gauss.

It has been shown that, for the three substances under investigation, the magnetic rotation is controlled by one absorption band in the ultra-violet, and so the magnetic rotary dispersion of each of the three liquids is represented by equations of the type

$$n\delta = K_1 \frac{\lambda^2}{(\lambda^2 - \lambda_1^2)^2}, \quad \dots \dots \dots (2)$$

where n is the refractive index and δ = Verdet's constant for a wave-length λ , K_1 is a constant, and λ_1 the wave-length of the absorption band in the ultra-violet.

The natural dispersion of a substance can be accurately represented, when not too near an absorption band, by an equation of the Ketteler-Helmholtz type, namely

$$n^2 - 1 = b_0 + \frac{b_1}{\lambda^2 - \lambda_1^2} + \frac{b_2}{\lambda^2 - \lambda_2^2} + \dots, \quad \dots \dots (3)$$

where n is the refractive index for a wave-length λ , b_0 , b_1 , b_2 , ... are constants, and λ_1 , λ_2 , ... are the wave-lengths of the absorption bands of the substance.

* *Loc. cit.* p. 490.

† *Loc. cit.*

If the assumption is now made that the natural dispersion is controlled by the same absorption band as is responsible for the magneto-optical dispersion, equation (3) reduces to

$$n^2 - 1 = b_0 + \frac{b_1}{\lambda^2 - \lambda_1^2}, \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (4)$$

which, on differentiation, gives

$$n \frac{dn}{d\lambda} = - \frac{\lambda b_1}{(\lambda^2 - \lambda_1^2)^2} \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (5)$$

Substituting (5) in (1), we get

$$\delta = - \frac{e}{2mc^2} \cdot \frac{\lambda^2 b_1}{n(\lambda^2 - \lambda_1^2)^2} \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (6)$$

Equating (6) and (2)

$$\frac{e}{m} = - \frac{2K_1 C^2}{b_1} \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (7)$$

The constant b_1 is determined from equation (4) by taking two values of the wave-length, say λ and λ' , and the corresponding values of the refractive index n and n' , and substituting.

Methyl Propionate.

	Wave-length in cm.	Refractive index.
(a)	6678×10^{-8}	1.375_5
(b)	5876×10^{-8}	1.377_7
(c)	5105×10^{-8}	1.380_7
(d)	2777×10^{-8}	1.415_3
(e)	2724×10^{-8}	1.417_5
(f)	2708×10^{-8}	1.418_5

Then

$$n'^2 - n^2 = b_1 \frac{\lambda^2 - \lambda'^2}{(\lambda^2 - \lambda_1^2)(\lambda'^2 - \lambda_1^2)} \cdot \quad \cdot \quad \cdot \quad \cdot \quad (8)$$

The value of b_1 calculated from (8) and the value of K_1 calculated from (2) in the correct units are substituted in (7),

and so $\frac{e}{m}$ is determined.

In the calculation of b_1 several pairs of values of the wave-length and the corresponding refractive indices were employed, and the mean value obtained was substituted in equation (7). The value of λ_1 used was that obtained from the magneto-rotary experiments.

Substituting the values

(a) and (f) in the equation (8), we get $b_1 = 8.6751 \times 10^{-11}$.

(c) and (f) „ „ „ $b_1 = 8.7281 \times 10^{-11}$.

(b) and (e) „ „ „ $b_1 = 8.6123 \times 10^{-11}$.

(a) and (d) „ „ „ $b_1 = 8.7024 \times 10^{-11}$.

Mean value of $b_1 = 8.68 \times 10^{-11}$.

Substituting the mean value of b_1 and the value of K_1 , which has been adjusted so as to fit equation (2) when δ is measured in radians/cm. gauss, in equation (7) we get

$\frac{e}{m} = 0.96 \times 10^7$, where e is in e.m.u.

Ethyl Propionate.

	Wave-length in cm.	Refractive index.
(a)	6678×10^{-8}	1.382_9
(b)	5876×10^{-8}	1.385_1
(c)	5049×10^{-8}	1.389_0
(d)	3158×10^{-8}	1.411_9
(e)	3046×10^{-8}	1.415_0
(f)	2951×10^{-8}	1.418_2

Substituting the values

(a) and (f) in the equation (8), we get $b_1 = 9.0395 \times 10^{-11}$.

(a) and (d) „ „ „ $b_1 = 8.9664 \times 10^{-11}$.

(b) and (e) „ „ „ $b_1 = 8.9875 \times 10^{-11}$.

(c) and (f) „ „ „ $b_1 = 8.9801 \times 10^{-11}$.

Mean value of $b_1 = 8.99 \times 10^{-11}$.

As previously explained, we deduce from equation (7) that the value of $\frac{e}{m} = 0.99 \times 10^7$, where e is in e.m.u.

Ethyl Formate.

	Wave-length in cm.	Refractive index.
(a)	6678×10^{-8}	1.360_6
(b)	5876×10^{-8}	1.362_8
(c)	4490×10^{-8}	1.369_7
(d)	2973×10^{-8}	1.392_3
(e)	2818×10^{-8}	1.397_8
(f)	2877×10^{-8}	1.396_0

Substituting the values

(a) and (e) in equation (10), $b_1 = 8.3540 \times 10^{-11}$.

(b) and (f) „ „ $b_1 = 8.2744 \times 10^{-11}$.

(c) and (d) „ „ $b_1 = 8.2747 \times 10^{-11}$.

Mean value of $b_1 = 8.30 \times 10^{-11}$.

On substituting the values of b_1 and K_1 in equation (7), we find that the value of $\frac{e}{m} = 0.996 \times 10^7$, where e is in e.m.u.

Natural Dispersion.

The approximate agreement in the values of b_1 , calculated for each liquid from different values of n and λ , indicates that the natural dispersion of each liquid is represented within experimental error by an equation of the type

$$n^2 - 1 = b_0 + \frac{b_1}{\lambda^2 - \lambda_1^2},$$

where λ_1 is the wave-length of the absorption band calculated from the results of the magneto-optical dispersion experiments.

The natural dispersion of methyl propionate over the range of wave-length from 0.6678μ to 0.2708μ is represented within experimental error by the equation

$$n^2 - 1 = 0.8716_7 + \frac{8.68 \times 10^{-3}}{\lambda^2 - (0.1066)^2},$$

where n is the refractive index for a wave-length λ measured in microns, and 0.1066μ is the wave-length of the ultra-violet absorption band deduced from the magnetic rotation experiments.

The natural dispersion of ethyl propionate over the range 0.6678μ to 0.2951μ , and of ethyl formate over the range 0.6678μ to 0.2670μ , is represented by the equations

$$n^2 - 1 = 0.8917_7 + \frac{8.99 \times 10^{-3}}{\lambda^2 - (0.1075)^2}$$

and

$$n^2 - 1 = 0.8323_0 + \frac{8.30 \times 10^{-3}}{\lambda^2 - (0.1061)^2} \text{ respectively.}$$

The following tables give a comparison between values of the refractive index obtained experimentally and those calculated from the above equations :—

Methyl Propionate.

Wave-length in microns.	n (calculated).	n (observed).
·5893	1·377 ₇	1·377 ₇
·4550	1·384 ₀	1·384
·3523	1·395 ₄	1·395
·2854	1·412 ₆	1·412 ₂

Ethyl Propionate.

Wave-length in microns.	n (calculated).	n (observed).
·5893	1·385 ₁	1·385
·4500	1·392 ₆	1·392 ₅
·3444	1·405 ₅	1·405 ₃

Ethyl Formate.

Wave-length in microns.	n (calculated).	n (observed).
·5893	1·362 ₈	1·362 ₇
·4465	1·369 ₈	1·369 ₈
·3678	1·378 ₀	1·377 ₅
·3232	1·386 ₁	1·385 ₅

The values of the refractive indices calculated from the dispersion equations agree with the observed values within experimental error in their determination. These equations, however, may require modification when more accurate values of the refractive indices are available.

DISCUSSION OF RESULTS.

The magneto-optical dispersion of ethyl formate and of methyl and ethyl propionate over the range of spectrum extending from about $·45\mu$ to about $·30\mu$ can be represented by the equation

$$n\delta = K_1 \frac{\lambda^2}{(\lambda^2 - \lambda_1^2)^2},$$

where δ and n are the values of Verdet's constant and the refractive index of the liquid for a wave-length λ , K_1 a

constant which varies from liquid to liquid, and λ_1 the wave-length corresponding to the free period of the resonators. The values of λ_1 and K_1 for the three liquids are given in the accompanying table. The values of Verdet's constant (for sodium light) of each liquid calculated from the magneto-optical dispersion equations, together with the values determined experimentally by Perkin for ethyl formate and ethyl propionate, are also included in the table.

Liquid.	λ_1 , microns.	K_1 *.	Verdet's constant calculated for sodium light.	Verdet's constant observed by Perkin.
Ethyl formate ($\text{HCO}_2\text{C}_2\text{H}_5$)	0.1061	4.72×10^{-3}	0.0106 ₅ (14.8° C.)	0.0106 ₄ (14.8° C.)
Methyl propionate ... ($\text{C}_2\text{H}_5\text{CO}_2\text{CH}_3$)	0.1066	$4.771_5 \times 10^{-3}$	0.0106 ₅ (17.1° C.)	
Ethyl propionate ... ($\text{C}_2\text{H}_5\text{CO}_2\text{C}_2\text{H}_5$)	0.1075	5.068×10^{-3}	0.0112 ₇ (15.8° C.)	0.0112 ₆ (15.7° C.)

* The values of K_1 correspond to δ measured in min. per cm. gauss.

The experimental results show that over the range of wave-lengths investigated the magnetic rotations can in the case of each liquid be represented by a formula involving only one free period, and also the values of Verdet's constant for sodium light calculated from the magneto-optical dispersion equations of ethyl formate and ethyl propionate are in good agreement with the values determined experimentally by Perkin. It is also evident from the results given in the above table that the values of both λ_1 and K_1 increase with an increase in the molecular weight of the liquid examined.

The natural dispersion of ethyl formate and of methyl and ethyl propionate from $.6678\mu$ to about $.2700\mu$ can be represented by an equation of the type

$$n^2 - 1 = b_0 + \frac{b_1}{\lambda^2 - \lambda_1^2},$$

where λ_1 is the wave-length of the absorption band in the ultra-violet calculated from the magneto-optical experiments. The values of the constants b_0 and b_1 increase with the

molecular weights of the liquids. The values of $\frac{e}{m}$ obtained

by combining the results of the magnetic rotation experiments with those relating to ordinary dispersion are practically the same for the three liquids, but decidedly lower than the

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accepted value. The values obtained for ethyl formate, methyl propionate, and ethyl propionate were $\cdot996 \times 10^7$, $\cdot96 \times 10^7$, and $\cdot99 \times 10^7$ e.m.u. respectively. Other investigators have obtained similar results from magneto-optical and natural dispersion experiments.

SUMMARY.

(a) The magneto-optical rotation of methyl propionate, ethyl propionate, and ethyl formate has been determined for various wave-lengths in the region of the spectrum extending from $\cdot4500 \mu$ to about $\cdot3000 \mu$.

The refractive indices of the same liquids have also been determined for wave-lengths between $\cdot6678 \mu$ and about $\cdot2700 \mu$.

(b) The magneto-rotary dispersion of the three liquids can be represented by equations of the type

$$n\delta\lambda^2 = K_1 \left\{ \frac{\lambda^2}{\lambda^2 - \lambda_1^2} \right\}^2,$$

where n and δ are the refractive index and Verdet's constant for wave-length λ , K_1 a constant depending on the liquid investigated, and λ_1 the wave-length of the absorption band.

The values of λ_1 for methyl propionate, ethyl propionate, and ethyl formate are $\cdot1066 \mu$, $\cdot1075 \mu$, and $\cdot1061 \mu$ respectively.

(c) The ordinary dispersion of the three liquids can be represented within experimental error by equations of the type

$$n^2 - 1 = b_0 + \frac{b_1}{\lambda^2 - \lambda_1^2},$$

where b_0 and b_1 are constants and λ_1 is the wave-length of the absorption band determined from the magnetic rotation experiments.

(d) The values of $\frac{e}{m}$ for methyl propionate, ethyl propionate, and ethyl formate deduced from Larmor's theory of magneto-optical dispersion are $\cdot96 \times 10^7$, $\cdot99 \times 10^7$, and $\cdot99_6 \times 10^7$ e.m.u. respectively.

XXIX. *A Thermal Theory of Cathodic Disintegration.* By H. P. WARAN, M.A., Ph.D., D.Sc., F.Inst.P., Professor of Physics, Presidency College, Madras*.

ABSTRACT.

THE thermal view advanced by the author to explain certain forms of disintegration observed in the glass walls of discharge-tubes is now extended to the case of the electrodes. Dealing with the sputtering of the cathode, the author has attempted an explanation of it as evaporation of small masses of metal under the localized intense heat of bombardment by the protons. Considering the sudden rise of temperature restricted to the immediate neighbourhood of the point of impact, it is found that the observed relative sputtering of metal is found to be explicable in terms of the thermal conductivity, density, boiling-point, and other physical properties of the metal.

THE phenomenon of disintegration observed in discharge-tubes has been a matter of experimental study as early as 1861, when Gassiot presented a report on the subject to the British Association. The observed disintegration may broadly be classified into two groups :—

- (a) the disintegration of the glass walls,
- (b) the disintegration of the electrodes;

and a study of both the types of disintegration is not only of scientific interest to us, but it is also a matter of great practical industrial importance, as the design and construction of X-ray tubes, discharge-tubes, and other allied devices are greatly dependent on the results of such study.

In two earlier publications on the subject † I have already summarized my observations on the study of the disintegration suffered by the glass walls of a discharge-tube. To accentuate the action, when a strong magnetic field is applied transverse to the path of the discharge, the discharge that is deflected on to the glass walls is found to have caused on the glass surface a series of fine cracks or

* Communicated by the Author.

† Phil. Mag. xliii. p. 226 (1922); xlv. p. 305 (1923).

grooves, these grooves sometimes converging in the direction in which the current is flowing. At first an explanation was sought for this curious phenomenon in terms of a mechanical theory of origin for these convergent grooves. They were considered as furrows dug up by the deflected massive positive particles. Further observations on the phenomenon led to a modification of this view, and this type of disintegration was accounted for on the basis of a thermal theory. The deflected discharge presents a striated appearance, and causes intense local heating of the glass. This may suffice to effect a surface fusion of the glass which, on cooling, leads to a number of fine surface-cracks on the glass, the mechanical effect, if any, of the positive particles playing only a minor rôle.

In the present paper it is proposed to deal with the second type of disintegration, namely, that at the electrodes, and apply this thermal theory to explain some of the observed facts. The subject of cathodic sputtering, as the disintegration of the cathode is called, has already received a great deal of attention at the able hands of Sir William Crookes *, Kohlschuller †, the research staff of the General Electric Company ‡ and many others. Restricting ourselves to the cathode where the observed disintegration or sputtering is greatest, we find that as early as 1891 Sir William Crookes § arranged some of the metals in the order in which they suffered disintegration when used as the cathode in a discharge-tube, and tried to find a relation between the observed values of relative sputtering and any of the other constants of the metal such as density, atomic weight, etc., without any result. He considered the sputtering as electrical evaporation, and had also noted that a higher temperature of the electrode was conducive to its rapid disintegration, though the melting-point of the metal seemed to have no relation to the extent of the disintegration observed.

In the proposed thermal explanation for the observed facts of cathodic disintegration the disintegration is supposed to be due to the evaporation of the metal under the heat of bombardment of the positive rays, the purely mechanical effect, if any, being smaller than the thermal

* Proc. Roy. Soc. l. p. 88 (189).

† *Jahrb. d. Rad. W. Elect.* ix. p. 355 (1912).

‡ Phil. Mag. xlv. p. 98 (1923).

§ Proc. Roy. Soc. l. p. 88 (1891).

effect. The evaporation of metal is not due to the gradual rise of temperature of the whole mass of metal of the cathode. It is rather due to the practically or very nearly instantaneous evaporation of the small mass of metal in the immediate neighbourhood of the point of impact. Dealing with a small number of bombarding particles and the very small superficial mass of metal affected by them, it is easy to see that the loss of energy might be sufficient to completely evaporate a small mass of the metal at the low pressure of the surrounding gas. The vaporized metal would condense on the neighbouring walls of the tube and electrode, which are at a very much lower temperature. That this type of surface-fusion does occur in discharge-tubes is supported by the observed phenomenon of the fusion of a small area of the anti-cathode (focal spot) of an X-ray tube even when the interval for which current is on as short as $1/100$ sec. and the metal is backed all the time by a large mass of conducting metal intended to conduct any heat generated locally. We can also observe in discharge-tubes on the surface of the cathode a number of bright scintillations which can be regarded as due to the mass of metal being raised to a white-heat at the point.

A general consideration of all the influences at work that determine the rise of temperature of a given mass of metal subjected to this bombardment leads us to the conclusion that the following factors, for the reasons discussed under each, should have a bearing on the observed mass sputtered.

(1) *Thermal Conductivity of the Metal.*

It is obvious that as the bombarded mass rises in temperature, the heat is being rapidly conducted away by the adjoining mass of metal, and the final temperature attained by the bombarded mass of metal would be determined by the rate of loss of heat, mainly due to conduction (that lost by radiation being neglected). If this had any serious bearing on the observed sputtering we should find metals of low-heat conductivity like palladium, lead, and platinum showing a very much higher sputtering than metals of higher conductivities like magnesium, aluminium, and copper. Experimentally-observed values for relative sputtering are in general support of this view, as can be seen from Table I.

(2) *The Thermal Conductivity of the Surrounding Gas.*

We should also expect that the gas surrounding the region bombarded would abstract from the metal a part of the heat which would be conducted away. Hydrogen and

TABLE I.

Metal.	Specific heat.	Density.	Thermal conductivity.	Melting-point.	Boiling-point.	Sputtering.
1. Palladium	·06	11·4	·182	1550	2540	108
2. Gold	·03	19·32	·703	1063	2530	100
3. Silver	·05	10·00	·992	962	1955	82
4. Lead	·03	11·37	·082	327	1525	75
5. Tin	·05	7·29	·145	232	2270	57
6. Platinum	·03	21·50	·173	1710	2450	44
7. Copper	·09	8·93	·908	1084	2310	40
8. Cadmium	·05	8·64	·216	321	778	32
9. Nickel.....	·11	8·90	·138	1452	2330	11
10. Iron	·11	7·86	·150	1530	2450	5·5
11. Magnesium.....	·25	1·74	·376	633	1120	1
12. Aluminium.....	·22	2·70	·492	657	1800	0

helium of large heat-conductivity should have a marked tendency to keep down the temperature-rise because of their higher conductivity, and we should expect the sputtering observed in these gases to be correspondingly low. Table II. tabulates the observed result, which is quite in keeping with what we should expect on this theory.

TABLE II.

Gas.	Specific heat.	Thermal conductivity.	Density.	Sputtering.
1. Hydrogen	·34	36·9	1	·0025
2. Helium.....	·235	33·9	2	·003
3. Nitrogen	·235	5·24	14	·024
4. Argon	·123	3·89	40	·05

(3) *The Specific Heat of the Metal.*

For a given energy of bombardment equal masses of two metals would differ in temperature even if their heat-conductivity were the same. The metals of low

specific heats, like gold, silver, platinum, lead, etc. should show a very much greater sputtering than metals of higher specific heat like nickel, iron, magnesium, and aluminium, a result quite in keeping with the observed relative sputtering tabulated in Table I.

(4) *Specific Heat of the Surrounding Gas.*

The absorption of part of the energy by the surrounding gas to raise its own temperature must necessarily diminish the amount of energy available for raising the temperature of the metal, and the heat thus lost should depend on the specific heat of the gas. We should find in gas of high specific heat like hydrogen that the sputtering would be very much less than that observed with gases of low specific heat like nitrogen, and again a result in accordance with the observed values as tabulated in Table II.

(5) *Pressure of Gas surrounding the Electrode.*

We should expect the pressure of the gas to influence the result in very many ways. Though the thermal conductivity of gas remains independent of its pressure, yet at low pressures below about 5 mm. it begins to decrease, the decrease being quite rapid at about 1 mm., and this phenomenon has been used by Piram, Hale, Campbell *, and others for the measurement of low gas pressures. It is exactly over this range of pressure, when the conductivity varies most, that we find the sputtering also to vary very greatly. Owing to the decreased conductivities, as a result of the decreased pressure, we should expect the sputtering to increase with a decrease in pressure, a result experimentally confirmed. The pressure could also exercise a mass effect. As the pressure goes down, the mass of gas in the immediate neighbourhood of the bombarded area decreases, and the loss of heat absorbed by it in raising its own temperature also decreases. That should also contribute to the observed increase in sputtering as the pressure is reduced.

(6) *The Density of the Metal.*

The density of the metal may be expected to exert an appreciable effect, since we are considering a case of energy

* Proc. Phys. Soc. xxxiii. p. 287 (1921).

transfer taking place over a small area in a short time. Considering equal masses of two metals differing largely in density, one could see that the whole of the mass of higher density could be available within a very much shorter radius of the bombarded spot than an equal mass of metal of lower density. Thus we should expect in such quick transfer of energy the mass of higher density to attain a higher temperature, leading to a greater evaporation, than an equal mass of lower density. Thus dense elements like gold, platinum, silver, and lead should show a very much higher sputtering than light elements of the magnesium and aluminium type. A reference to Table I. would show that the experimentally-observed values of relative sputtering are in conformity with this expectation.

(7) *The Boiling-point of the Metal.*

The metal has to be raised to such a high temperature as to boil it off the surface, and one can expect for a given amount of energy that a metal of lower boiling-point should be sputtered off far more easily than a metal of very much higher boiling-point. Thus an easily boiling metal like cadmium should sputter relatively much more than a metal of much higher boiling-point like magnesium or aluminium. Similarly, lead and silver ought to show a much higher sputtering than iron or platinum. These results are also confirmed by the figures of Table I.

(8) *The Latent Heat of Evaporation of the Metal.*

Since energy has to be supplied even after the metal particle has been taken right up to the boiling-point, to enable it to boil off, a metal of high latent heat of vaporization would require a lot more heat than an equal mass of lesser heat, and hence the metals of lower latent heat ought to show a higher sputtering than metals of higher latent heat. Data on this point are lacking, and it is difficult to conclude what evidence there is in support of our view on this point. Perhaps, when the interrelation of all these variables become clear, it may be possible to determine the latent heat of vaporization of metals by this method of sputtering.

(9) Effect of Different Gases and Different Metals.

In general the sputtering is found to vary with metals and also with the surrounding gas. We have found that, since the sputtering is dependent on the individual properties of the metals and gases that differ amongst themselves so widely, the observed variation is only to be expected if this thermal theory has any basis of truth in it.

(10) Current Strength.

The number of protons or the strength of current determine the rate at which energy is being imparted by collisions to the cathode, and we should expect the observed sputtering to increase with it. This is found to be the case experimentally.

(11) Effect of Potential across the Tube.

The energy of each proton would depend on the driving potential, and we should expect the sputtering to increase with the applied P.D., the current and other factors remaining the same. This again is an experimental result in support of our view.

(12) Mechanical Effects and other Variables.

There is nothing unnatural in the supposition that the bombardment of a metallic surface by a shower of fine particles like the positive rays might result in a certain amount of mechanical sand-blast action on the surface by which aggregates of particles are bodily torn from the surface. There is also nothing to prevent our pursuing this mechanical idea further and supposing that a certain amount of splashing about of the molten mass of metal occurs as a result of the supposed bombardment by particles on an area that has just melted as a result of previous bombardments. In this way the melting-point of the metal also enters as an additional variable affecting the result. The extent of the disintegration attributable to this cause will depend largely on the physical properties of the surface in question, such as its hardness, elasticity, roughness, etc., and it would be very difficult to estimate it. But, physically speaking, we can see that soft metals like lead, silver, and gold should show a very much higher

sputtering than hard metals like nickel and iron, and this is found to be the case experimentally.

On all these twelve counts one can see that there is a certain volume of quantitative evidence in support of this purely thermal view for the observed cathodic disintegration. There are probably other variables, in addition to the dozen or so I have enumerated in support of the thermal view. Apparent exceptions to the expected behaviour are quite numerous, and one can pick up a few from Table I. But it must be remembered that the data given in Table I. for relative sputtering are far from accurate for all the metals, since in an experiment involving over twelve variables it is difficult, if not impossible, to ensure uniformity of conditions throughout the determinations of sputtering by experiment.

In a complex phenomenon of this nature, where the variables and disturbing factors are so many and their interaction so uncertain, we cannot expect to find at once a quantitative relation between the various factors. The slightest impurity in the gas or metal may produce great changes in thermal conductivity, boiling-point, etc., at low pressures. Thus by the addition of zinc to copper, if we lower its conductivity from $\cdot 9$ to $\cdot 26$, the boiling-point also suffers a great diminution, and the sputtering increases from 40 to 51. Thus at best at this stage we can only trace a qualitative agreement, making ample allowances for the diverse factors involved. Even to such an experiment there are apparent exceptions. Thus, platinum and iron, though of nearly the same conductivity and boiling-point, show a great difference in sputtering, the platinum sputtering about 8 times as much as iron. But it must be noted that the specific heat of platinum is only $\frac{1}{3}$ that of iron, and that may account for 3 times the sputtering of iron. Again, the density of platinum is $2\frac{1}{2}$ times that of iron, and with that we can account for the $3 \times 2\frac{1}{2} = 8$ times the sputtering of iron which platinum has. Still, we cannot ignore exceptions that cannot be explained away so easily by taking the combined effect of two or three of the most important variables. While some of these may be real exceptions, many of them may turn out to be only apparent ones, clearing away as soon as the doubtful constants and data concerned are accurately determined by further work.

XXX. *Contribution to the Theory of Dielectrics.* By G. GUÉBEN, *Docteur en Sciences, Chef de travaux à l'Université de Liège* *.

NUMEROUS theories have already tried to explain the phenomena observed in dielectrics—dielectric absorption, production of heat in alternating fields, variation of the dielectric constant according to the duration of charge or to the frequency. One of these theories offers several points of concordance with connected studies: this is specially the case with the dipole theory which has been lately developed by S. Whitehead †. There is, however, a particular point which the above-mentioned theories do not explain—the residual conductivity of dielectrics, *i.e.*, the conductibility which persists even after the field has remained applied for a rather long time, and the variation of this conductivity under the action of penetrating radiations, X-rays or radium-rays. We all know that a theory based upon an ionic conductivity of dielectrics has been offered ‡. But several authors have proved the impossibility of explaining the other anomalous properties of dielectrics by means of this theory. The experimental work of Helmut Neumann § has induced him to suggest two distinct causes of all the observed phenomena: (1) the presence of dipoles which produce the anomalous properties of dielectrics; (2) the presence of charged particles, such as ions, the removal of which would provoke the conduction current, and the number of which would be increased by the penetrating radiations according to a process similar to that known as ionization.

We have had the opportunity, while investigating the action of radium-rays on solid dielectrics, of searching what are the laws of the ionization of solid dielectrics ||. There is no reason to suppose that ions produced under the action of penetrating radiations behave otherwise than ions pre-existent to the action of these radiations, and due probably to the action of some causes such as the ultrapenetrating radiations.

* Communicated by the Author.

† S. Whitehead, *Phil. Mag.* ix. p. 865 (1930).

‡ An account of all these theories will be found particularly in v. Schweidler, *Ann. der Physik*, xxiv. p. 711 (1907); J. B. Whitehead, 'Diélectriques et isolants. Théories et expériences' (Paris, Chiron (1928)).

§ Helmut Neumann, *Z. S. für Physik*, xlv. p. 717 (1927).

|| G. Guében, *Mémoires de l'Ac. R. de Belgique*, xi. (1930).

It seemed interesting to publish a synthesis of the theoretical results obtained, on the one hand, by the dipole theory, and, on the other hand, by our own experimental works.

Dipole Theory.

A field H produces in a dielectric of dielectric constant or specific inductive capacity μ an electric displacement

$$D = \frac{\mu H}{4\pi}, \quad (1)$$

productive of a current

$$i_1 = \frac{dD}{dt}. \quad (2)$$

In the present case H is constant, μ a function of time t that S. Whitehead has expressed as follows :

$$2 + \mu = 3 \left\{ 1 - b - a \left(1 - e^{-\frac{2tKT}{\rho}} \right) \right\}, \quad . . . (3)$$

in which

$$a = \frac{4\pi m^2 N}{9KT}. \quad (4)$$

K = Boltzmann's constant,

m = dipole moment,

T = absolute temperature,

N = number of dipoles per c.c.,

ρ = frictional resistance coefficient of the medium,

b = a corrective term for the polarization arising from other causes than dipoles.

Consequently the current per unit of surface is given by

$$\begin{aligned} i_1 &= \frac{H}{4\pi} \cdot \frac{d\mu}{dt} \\ &= \frac{H}{4\pi} \frac{6KTa}{\rho} e^{-\frac{2tKT}{\rho}} \left\{ 1 - b - a \left(1 - e^{-\frac{2tKT}{\rho}} \right) \right\}^2. \end{aligned} \quad (5)$$

To obtain this result, the secondary fields due to the action of the neighbouring molecules have been supposed to be added to the external field, so as to produce the whole inducing field. Supposing that the external field acts alone on the dipoles, we shall obtain the more simple formula

$$\mu = 1 + b + a \left(1 - e^{-\frac{2tKT}{\rho}} \right), \quad (6)$$

whence
$$i_1 = \frac{aHKT}{2\pi\rho} e^{-\frac{2eKT}{\rho}} \dots \dots \dots (7)$$

We thus obtain a simple exponential function, similar to the function deduced from Pellat's theory or kindred theories.

Conduction in the Dielectric.

Our study of the ionization of solid dielectrics has led us to admit that the law of recombination of ions is linear

$$\frac{dn}{dt} = q - \alpha'n. \dots \dots \dots (8)$$

This is logical, considering that the ionization is smaller than in a gas and that the solid constitution of the medium leads to the presence of numerous adsorption nuclei; we find here conditions similar to those observed by von Schweidler*, Nolan and Enright†, and Power‡ when studying the slightly ionized gases, and specially when studying the atmospheric ionization.

If we thus accept the law of recombination (8), and if we take into account the fact that the amount of ions removed through the field is proportional to their number, we may state that, when the field acts, we obtain

$$\frac{dn}{dt} = q - \alpha'n - \beta n, \dots \dots \dots (9)$$

$\alpha'n$ representing the number of ions disappearing through recombination and βn the number of ions brought to the electrodes under the action of the field.

We may also write

$$\frac{dn}{dt} = q - \beta'n, \dots \dots \dots (10)$$

in which

$$\beta' = \alpha' + \beta. \dots \dots \dots (11)$$

The integration of the equations (10) leads in the general case to

$$n_t = \frac{q}{\beta'}(1 - e^{-\beta't}) + n_0 e^{-\beta't}. \dots \dots \dots (12)$$

* Von Schweidler, *Wien. Ber.* cxxvii. p. 953 (1918); cxxviii. p. 917 (1919); cxxxiii. p. 23 (1924).

† Nolan, and Enright, *Proc. Roy. Irish Acad.* xxxvi. p. 93 (1923).

‡ Power, *Journ. Frankl. Inst.* p. 327 (1923).

The fraction of the current observed produced by the ions is given by

$$i = n\epsilon(u+v)Hs, \quad (13)$$

ϵ being the charge of an ion, u and v the mobilities respectively of positive and negative ions, H the field, s , the section of the current.

We thus obtain

$$i_t = \frac{\epsilon(u+v)Hs}{\beta'} [q(1 - e^{-\beta't}) + \beta'n_0 e^{-\beta't}]. \quad (14)$$

In this formula n_0 represents the initial number of ions; it is the number of ions present in the stationary state, before the application of the field. The equation (8) gives

$$n_0 = n_1 = \frac{q}{\alpha'}. \quad (15)$$

If we suppose, for a moment, that at the initial time chosen we suppress the rays-source, we shall have for $t=0$, $q=0$, and the preceding equations become

$$\frac{dn}{dt} = -\beta'n, \quad (16)$$

$$n_t = n_0 e^{-\beta't}, \quad (17)$$

$$i_t = \epsilon(u+v)Hsn_0 e^{-\beta't}. \quad (18)$$

I have been able to show* that the equation (18) represents the curve of decrease of the current in the dielectric when, field and rays-source having acted for a sufficiently long time, the source of ionization is eliminated. In this case the initial state of equilibrium is characterized, according to equation (10), by

$$n_0 = n_2 = \frac{q}{\beta'}, \quad (19)$$

and the current is given by

$$i_t = \epsilon(u+v)Hsn_2 e^{-\beta't}. \quad (20)$$

If we now try to establish the quantity of electricity carried to the electrodes by the current from the moment when we eliminate the source to the moment when the supplementary ionization current is cancelled, we obtain

$$\begin{aligned} Q &= \int_0^{\infty} i_t dt = \epsilon(u+v)Hsn_2 \int_0^{\infty} e^{-\beta't} dt \\ &= \frac{\epsilon(u+v)Hsn_2}{\beta'}. \end{aligned} \quad (21)$$

* G. Guében, *loc. cit.*

On the other hand, if we keep in mind that the charges are exclusively carried to the electrodes through the βn ions removed by the current per c.c. and per second, we also have

$$Q = \int_0^\infty \beta n_t \epsilon \omega dt = \int_0^\infty \beta \epsilon \omega n_2 e^{-\beta t} dt \\ = \frac{\beta \epsilon \omega n_2}{\beta'}, \quad . \quad . \quad . \quad . \quad (22)$$

ω being the volume of the current.

From the equations (21) and (22) we can deduce

$$\beta = \frac{H(u+v)}{l}, \quad . \quad . \quad . \quad . \quad (23)$$

l being the thickness of the dielectric,

$$l = \frac{\omega}{s}. \quad . \quad . \quad . \quad . \quad (24)$$

As the preceding formulæ apply to the ionization current produced in the dielectric under the action of an external cause (as, for instance, radium-rays), they may evidently be applied to the ionization current which is always present in the dielectric and which is added to the current due to the polarization.

The Whole Current.

If we combine the results obtained, on the one hand, from the dipole theory and those obtained, on the other, from the study of the ionization, we shall have for the whole current in the dielectric

$$I = \frac{aHKT}{2\pi\rho} e^{-\frac{2tKT}{\rho}} + \frac{\epsilon(u+v)H}{\alpha' + \frac{H(u+v)}{e}} \left[q(1 - e^{-\beta t}) + \frac{\beta' q}{\alpha'} e^{-\beta t} \right] \\ = \frac{aHKT}{2\pi\rho} e^{-\frac{2tKT}{\rho}} + \frac{q\epsilon(u+v)^2 H^2}{l\alpha'^2 + H(u+v)\alpha'} e^{-\beta t} + \frac{q\epsilon(u+v)Hl}{l\alpha' + H(u+v)}, \\ . \quad . \quad . \quad . \quad (25)$$

decreasing current which tends to the limit

$$I_\infty = \frac{q\epsilon(u+v)Hl}{l\alpha' + H(u+v)}, \quad . \quad . \quad . \quad . \quad (26)$$

which represents the final conduction current in the dielectric. We have not been in a position to compare the formula (25) with the experimental results, because of

the lack of several elements. This formula, however, seems to be in accordance with the facts observed. Indeed, several authors have expressed the current by the empiric formula $I = bt^{-n}$. In order to reconcile this empiric result with his theoretical studies, von Schweidler has expressed the current under the form of a sum of exponential functions, a form that we find here. Besides, Helmu Neumann has experimentally shown that, in the case of sulphur and amber, the current of charge was equal to the conduction current plus a sum of two exponential functions.

The formula (25) is no longer in opposition with the phenomena observed in the alternating fields; indeed, in such fields, in consequence of the slight mobility of the ions, the fraction due to the ionic current is negligible, if not null; hence the formula (25) is reduced to its first term, and S. Whitehead has shown that it could explain the phenomena observed in the alternating fields.

When establishing formula (25) we have employed the simplified formula (7) of the dipole theory. Evidently we might obtain a more precise result through a combination of the formula (5) and of the results of the ionic theory.

Summary.

We have supposed that the current in a dielectric is due both to the contribution of dipoles and to the presence of ions. We have determined the part due to each of these two elements, and we have found a formula which we can propose as the general expression of the current in a solid dielectric.

XXXI. *On the Distribution of Space-potential in High-frequency Glow Discharge.* By D. BANERJI, M.Sc., Lecturer in Physics, University College of Science, Calcutta, and R. GANGULI, M.A., M.Sc., Lecturer in Physics, Serampore College*.

Introduction.

DURING recent years the phenomenon of high-frequency glow discharge in gases has received a large amount of attention, due, probably, to the ease with which undamped electrical oscillations of frequencies of

* Communicated by Prof. S. K. Mitra, D.Sc.

several millions per second can be maintained in a valve oscillatory circuit. The investigations * on the subject are, however, mainly confined either to the measurement of the striking voltages for various pressures and frequencies or to the qualitative study of the nature of striations. A knowledge of the distribution of space-potential is of considerable interest and importance in understanding the nature and mechanism of the discharge phenomena. Though a number of measurements of space-potential have been carried out in the case of the D.C. discharge † in various gases, the corresponding measurements in the case of high-frequency A.C. discharge seem to be entirely wanting.

The present investigation was therefore undertaken to measure the space-potential in high-frequency discharge (frequency 10^6 cycles) in air and oxygen by adopting the "Exploring Collector" method recently developed by Langmuir and Mott-Smith ‡. The method has the advantage that, besides the space-potential, it yields information regarding the concentration of the electrons, their average velocity, and the electronic current density in the different parts of the discharge-tube. The results of such measurements are set forth and discussed in the present paper.

The "Exploring Collector" Method.

The theory of the "Exploring Collector" method has been fully discussed in a paper by Langmuir and Mott-Smith §. A brief and simplified résumé of the same in the commonly used case of a cylindrical "collector" will, however, be useful here.

The method is a modification of the old method of determining the potential at a point in a discharge-tube by inserting into it a probe-wire connected to an outside

* Gutton, Mitra, and Ylostalo, *Journ. de Physique*, ser. 6, 1923; Kirchner, *Ann. der Physik*, lxxvii. pp. 287-301 (1925); Richards, *Phil. Mag.* ii. pp. 508-11 (1926); Gill and Donaldson, *Phil. Mag.* ii. pp. 129-37 (1926); McCallum and Perry, 'Nature,' 1929; Hayman, *Phil. Mag.* vii. p. 586 (1929); Townsend and Nethercot, *Phil. Mag.* vii. p. 600 (1929).

† McCurdy, *Phil. Mag.* xlviii. p. 898 (1924); Bramley, *Phys. Rev.* xxvi. p. 794 (1925); McCurdy and Dalton, *Phys. Rev.* xxvii. p. 163 (1926); Emeléus and Harris, *Phil. Mag.* iv. p. 49 (1927).

‡ Langmuir and Mott-Smith, *Phys. Rev.* xxviii. p. 727 (1926).

§ *Ibid.* A discussion of the method is also to be found in 'Conduction of Electricity Through Gases,' Methuen's Monograph Series, by K. G. Emeléus.

electrometer *. The latter method was obviously based on the assumption that the supply of positive and negative ions in the gas was sufficient to enable them to give up their charges to the wire and thus raise or lower its potential to equality with the surrounding gas. But in a discharge-tube under low pressures, where great variations in the concentration of the positive and negative ions occur, the probe-wire, after being charged to a certain limit, will be repelling ions of similar kind, and its potential may be lower than that of the point where it is introduced.

In Langmuir's modification the potential of the probe-wire designated as "collector" is varied, and the corresponding volt-ampere characteristic for any particular point in the discharge is determined. In the uniform glow of a discharge-tube the carriers of electricity are the ions and the electrons. Thus, for very high negative values of the potential of the collector as referred to the potential of the space where it is introduced, the collector, by attracting a number of positive ions and repelling negative ions or electrons, becomes surrounded by a cylindrical positive ion-sheath of definite thickness. The potential just outside the sheath is the potential of the space. As the potential of the collector is gradually made less and less negative, so as ultimately to equal the potential just outside the sheath, the thickness of the sheath gradually diminishes, and vanishes when the two potentials are equalized. The current flowing to the collector in the latter case is the usual drift current due to electrons only, because, on account of the smallness of the mass, their mobility far exceeds that of the positive ions. For potentials of the collector much lower than that of the space, when a positive ion-sheath is formed round the collector the current is mainly due to the flow of positive ions on the outside of the sheath and partly to electrons which have sufficient energy to penetrate the retarding potential of the sheath; but this latter current gains in strength, neutralizes, and finally outweighs the effect of the positive current as the potential of the collector approaches the potential of the space.

Assuming Maxwell's law of distribution to hold for the thermal velocity of the electrons, let u and v be the radial and tangential velocities of the electrons round the sheath.

* J. J. Thomson, 'Conduction of Electricity through Gases,' p. 530.

The current per unit area to the collector when it has just attained the space potential is

$$i = N\epsilon \int_0^\infty \int_{-\infty}^\infty \frac{m}{2\pi kT} e^{-\frac{m}{2kT}(u^2+v^2)} du dv = N\epsilon \sqrt{\frac{kT}{2\pi m}}. \quad (1)$$

Here m is the mass of the electrons,

T is the temperature,

N is their number per c.c., and

ϵ is the charge.

Langmuir and Mott-Smith have discussed in their paper the effect of a drift superposed upon pure Maxwellian motion. For the purpose of high-frequency alternating-potentials, the drifting motion is to be replaced by an harmonic motion, which cancels out an effect of drift in every consecutive opposite phase of surging motion.

In order to calculate the electron current corresponding to a potential less than that of the space, we may simply take into consideration the difference of the electronic concentration between the inside and the outside of the sheath as set up by the retarding potential $V_0 - V$, where V_0 stands for the potential of the collector and V for that of the space outside. According to Boltzmann's distribution law, the ratio of the concentration of a system of particles at a temperature T at two places, where the differences in the potential energy of a particle is W , is given by

$$e^{-\frac{W}{kT}}.$$

Also, if \bar{V} is the voltage equivalent of the temperature of the electrons, $\epsilon\bar{V} = \frac{3}{2}kT$, where k is Boltzmann's constant.

The concentration ratio being thus expressible as

$$e^{-\frac{3}{2} \frac{V_0 - V}{\bar{V}}},$$

the current to the collector per unit area

$$I = N\epsilon \sqrt{\frac{kT}{2\pi m}} e^{-\frac{3}{2} \frac{V_0 - V}{\bar{V}}},$$

whence

$$\frac{d}{dV_0} (\log I) = -\frac{3}{2\bar{V}}. \quad . \quad . \quad . \quad . \quad (2)$$

Thus the logarithm of the electron current I plotted against the voltage V_0 of the collector will give a straight line so long as the space potential is not attained. The attainment of the space-potential by the collector accompanied by a failure of the above linear relation will be indicated by a sudden bend in the curve. The temperature of the electrons can be deduced from the slope of the straight line given by equation (2).

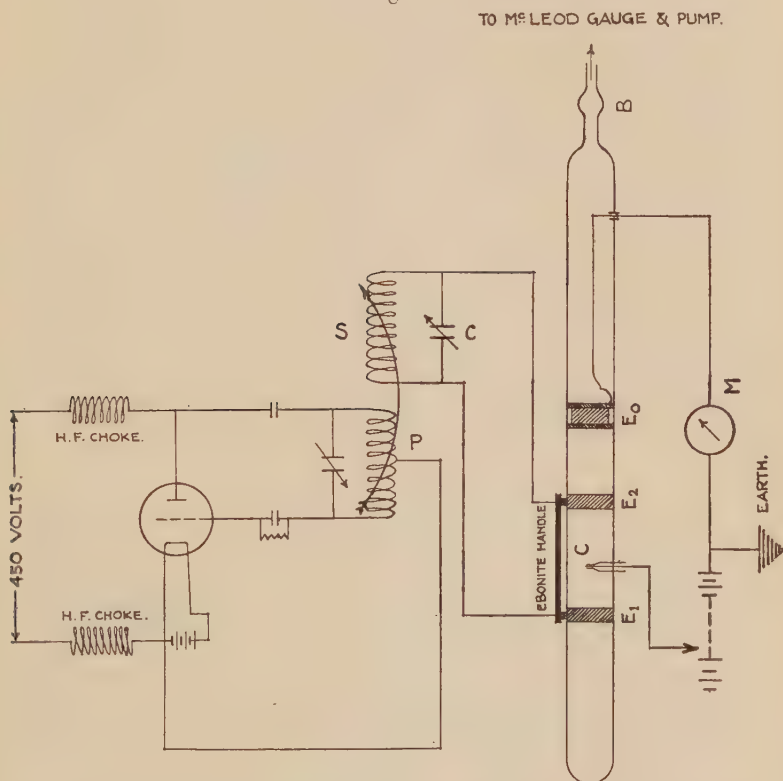
The current to the "collector" at various voltages as observed experimentally (Table I.) requires correction, according to the theory outlined above, for the presence in it of any positive ion current. The latter current is predominant for negative voltages of the collector, and slowly diminishes as the collector attains the potential of the space. This current per unit area can be expressed in terms of the thickness of the positive ion-sheath (D) and the mass of the ion (M) as $\frac{\sqrt{2}}{9\pi} \sqrt{\frac{\epsilon}{M}} V_0^{\frac{3}{2}} \frac{1}{D}$. By actual calculation its magnitude has been found to be of the order of 10^{-6} amp., and the corresponding electron current is never less than a few milliamperes in any case (Table I.) The correction is therefore negligibly small in comparison.

Experimental Arrangement and the Nature of Discharge.

The discharge-tube was cylindrical, being made out of a 80 cm. long Jena hard glass tube 3 cm. in diameter. It was sealed at one end and connected at the other to a McLeod gauge and a Cenco Hyvac pump. The details of the connexions are shown in fig. 1. The high-frequency E.M.F. was obtained from the terminals of the secondary coil S closely coupled to the primary coil P of a Hartley circuit; the coil S having a much larger number of turns compared to coil P , acted as a step-up transformer. The coil, when tuned with the help of the condenser C , developed peak-voltage up to 800 across its terminals. This was fed to the tube by two cylindrical external electrodes E_1, E_2 of copper foil, $\frac{1}{2}$ cm. wide, put round the discharge-tube. The "collecting electrode" C was a fine tungsten wire (radius .24 mm.) sealed inside a capillary cover and projecting radially inside the discharge-tube, so as to leave exposed to the discharge a collecting length of 5 mm., terminating at the centre of the section of the tube. As the "collector" was conveniently fixed in position,

different points within the discharge were made available to it by simultaneous movement of the external electrodes with the help of the connecting ebonite handle. The external electrodes used in feeding in the power, however, required an additional internal electrode for referring the space potential at any point of the discharge to it. This

Fig. 1.



was secured by a hollow iron bobbin, E_0 , 3 cm. in external diameter and 2 cm. long, tied to a flexible metal wire which came out through a seal at one end of the discharge-tube and was permanently earth-connected. The bobbin electrode was kept clear of the main discharge and the distance separating it from the nearest external electrode was adjusted to equality in all cases. The necessary movements of the bobbin were made by an outside magnet. The

contamination of the tube by mercury vapour from the McLeod gauge was prevented by putting a deposit of metallic sodium in the trap B (fig. 1). Apart from the various forms of striated discharge under high frequency E.M.F., a glow discharge almost free from striations could be obtained by suitable regulation of the discharge-current. In such a form of glow discharge, the phenomena presented have features which are symmetrical about the middle point between the electrodes. The electrodes act as though they are cathodes in the corresponding D.C. discharge. The negative glow, the Faraday dark space, and the positive column appear in succession on moving away from any of the electrodes. In the case of air the colour of the discharge near the electrodes is deep violet. It gradually fades away in the Faraday dark space, changing to abrupt red, which remains uniform throughout the positive column. In oxygen the colour of the positive column is bright red. The peculiarity of this type of discharge lies in the conical extension of the glow beyond the electrodes, like two convergent beams with their apexes turned away from the electrodes. These glows are separated from the electrodes by dark spaces in the region beyond the electrodes.

Procedure and Results.

In order to get the current corresponding to varying potentials of the "collector," the circuit of the collector is completed through a 100-volt battery and a Cambridge "L" type unipivot galvanometer (M, fig. 1), to the internal electrode. The battery voltage could be reduced by steps of 20 volts each from +100 to -100 volts by means of suitable tappings. The internal electrode, being earth-connected, the applied battery voltage measures the voltage of the collector. A few current-voltage data are shown in Table I., and are drawn with the logarithm of the current in fig. 2. The straight portion shows that the Maxwellian law is valid in this case. The space-potential corresponding to any position of the collector is determined from the portion of the bend (indicated by arrow in fig. 2) as obtained by the intersection of the straight portions immediately preceding and following the bends. In the determination of the space-potential it has been noted that, other factors remaining the same, the space potential at any point of the discharge is largely dependent upon the

pressure in the discharge-tube. It rises as the pressure is lowered and also to some extent as the pressure is increased

FIG. 2.

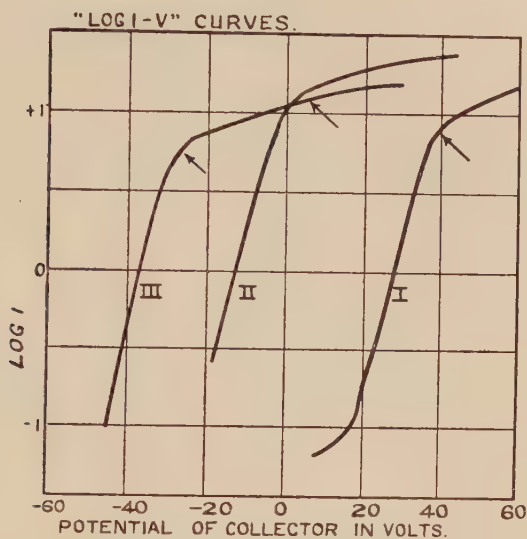
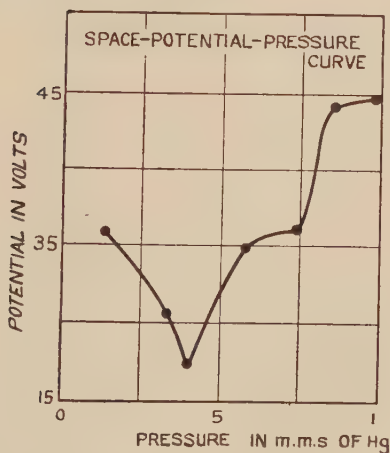


Fig. 3.



above a certain critical value. The variation is shown in fig. 3 for a point inside the positive column. It is referred to that of the earth, and has, therefore,

a constant difference with the maximum positive or negative value of the alternating potential of the electrodes. It

Fig. 4.

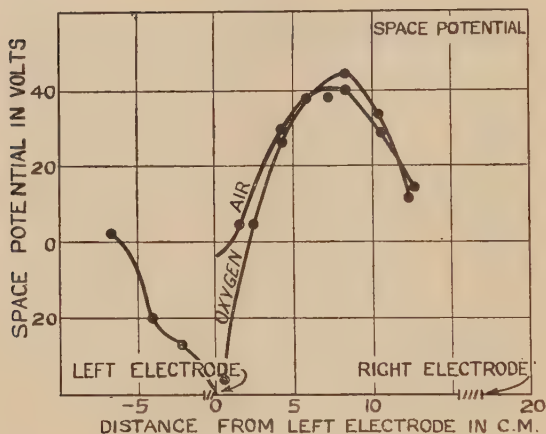


TABLE I.

Potential of Collector (volts).	Currents to Collector $\times 166$ (I amp./cm. ²).		
	I.	II.	III.
60	15.36	25.68	17.34
50	11.33	24.66	16.67
40	8.00	23.34	15.02
30	2.03	21.33	14.00
20	0.16	19.02	13.01
10	0.06	15.05	12.34
0	0.04	9.01	10.65
-10	0.00	2.00	9.32
	Current reversed.		Current reversed.
-20	0.32	1.02	7.02
-30	0.34	3.01	3.31
-40	..	3.33	0.40
			Current reversed.
-50	0.02

TABLE II.—In Air.

Distance between the electrodes, 7 cm.
 Pressure inside, 0.15 mm. of Hg.
 Discharge-current, 27×10^{-3} amp.
 Wave-length, 270 metres.

Distance from left electrode (cm.).	V. Space-potential (volts).	N. Concentration of electrons per c.c.	\bar{V} . Average electron velocity ($\sqrt{\text{volts}}$).	i . Current to "collector" at space-potential (amp./cm. ²).
2.3	40	1.10×10^8	20.27	2.55×10^{-3}
3.3	46	2.51×10^8	21.05	2.50×10^{-3}
4.3	42	2.39×10^8	15.00	2.02×10^{-3}
5.3	36	2.34×10^8	13.60	1.90×10^{-3}
6	30	1.61×10^8	12.90	1.27×10^{-3}

TABLE III.—In Air.

Distance between electrodes, 15 cm.
 Pressure inside, 0.14 mm. of Hg.
 Discharge-current, 15×10^{-3} amp.
 Wave-length, 270 metres.

Distance from left electrode (cm.).	V. Space- potential (volts).	Average electron velocity (cm./sec.).	N. Concentration of electrons per c.c.	i . Current to "collector" at space-potential (amp./cm. ²).
1.5	2	0.74×10^8	3.19×10^8	1.24×10^{-3}
4.5	22	0.79×10^8	4.09×10^8	1.76×10^{-3}
7.5	38	0.95×10^8	4.31×10^8	2.12×10^{-3}
8.5	40	1.03×10^8	4.72×10^8	2.52×10^{-3}
10.5	26	1.04×10^8	4.23×10^8	2.24×10^{-3}
12.5	14	1.00×10^8	3.45×10^8	1.76×10^{-3}

is to be observed that the potential distribution is symmetrical about the mid-point between the electrodes in the case when the discharge is free from striations (fig. 4).

It is maximum at the mid-point and falls off gradually on either side, to attain its minimum value inside the dark spaces near the electrodes. Beyond the electrodes it rises, to fall again to zero.

The concentration of the electrons in the various parts of the discharge-tube is given in Tables II., III., and IV. In

TABLE IV.—In Oxygen.

Distance between electrodes, 16 cm.

Pressure inside, 0.14 mm. of Hg.

Discharge-current, 21×10^{-3} amp.

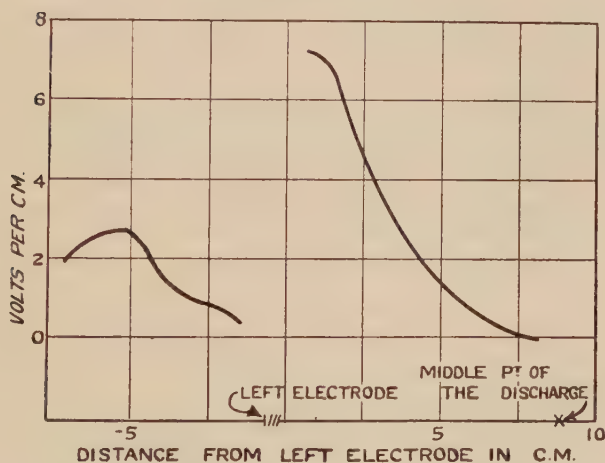
Wave-length, 270 metres.

Distance from left electrode (cm.).	V. Space- potential (volts).	\bar{V} . Average velocity of electrons ($\sqrt{\text{volts}}$).	N. Concentration of electrons per c.c.	i. Current to "collector" at space-potential (amp./cm. ²).
-5.5	2	18.70	0.48×10^8	0.45×10^{-3}
-3.5	20	10.87	1.24×10^8	0.89×10^{-3}
-1.5	26	7.83	1.66×10^8	1.01×10^{-3}
0.5	37	4.35	1.98×10^8	0.89×10^{-3}
2.5	4	5.09	2.39×10^8	1.22×10^{-3}
4.5	24	5.13	2.62×10^8	1.29×10^{-3}
6.5	37	5.21	2.76×10^8	1.39×10^{-3}
8.5	44	5.78	3.04×10^8	1.59×10^{-3}
10.5	32	5.21	3.26×10^8	1.59×10^{-3}
12.5	12	3.73	2.81×10^8	1.39×10^{-3}

common with the corresponding D.C. discharge, the main fall in potential is concentrated in the dark space near the electrodes, and the concentration of electrons there is less than that in other parts of the tube. The excess of positive ion concentration over negative ions at a point is derived from the slope of the curve drawn with the fall of potential per cm. against the distance from any electrode (fig. 5). An inspection of the curve shows that close to the electrodes, as well as in the middle of the positive column, the positive and the

negative ions are about equal in number. In the dark space, the concentration of positive ions is in excess. Qualitatively the influence of the external A.C. field is to concentrate the positive ions close to the electrodes and to drift out the electrons on account of their surpassing mobility. The glow in the positive column is maintained by the continual supply of electrons from the region just below the electrodes, the latter behaving as if they were both cathodes. Some of the outgoing electrons are, however, lost either by recombination with positive ions producing the characteristic negative glow or by diffusion towards the wall of the discharge-tube.

Fig. 5.



The extension of the dark space and the glow outside the region covered by the electrodes calls forth an explanation on similar lines.

As the motion of an electron in a high-frequency electric field is necessarily oscillatory, the half-cycle of alternation of the field must at least be equal to the period intervening between two successive collisions. The mean free path of an electron in oxygen at a pressure of .14 mm. of Hg is about 28 mm. This corresponds, according to the mean velocity found for them, to an interval of 2×10^{-9} sec. between two successive elastic collisions, and is, roughly, 1/200 of the period of half a cycle of the field. The maximum

influence of the field on the Maxwellian motion of an electron will thus operate at intervals of about 200 elastic collisions.

Summary and Conclusion.

The "exploring collector" method of Langmuir and Mott-Smith has been applied to study the space-potential distribution, ionic concentration, current density, and average electronic velocity in the case of high-frequency discharge through rarefied air and oxygen. It has been found that the potential distribution is symmetrical about the middle point of the discharge-tube, both the electrodes acting as cathodes in the corresponding D.C. discharge. The extension of the glow outside the electrodes is also a symmetrical reproduction of the phenomena inside, with the difference that after a certain length the potential gets reduced to zero.

In conclusion we offer our best thanks to Prof. S. K. Mitra for suggesting the problem and for his help and guidance during the course of the investigation.

Wireless Laboratory,
University College of Science,
Calcutta,
July 25, 1930.

XXXII. *On the Kinetics of the Oxidation of Copper: the Establishment of Sorption Equilibria.* By F. J. WILKINS*.

FROM the data provided by a study of the oxidation of copper (Proc. Roy. Soc. A, cxxviii. pp. 394 and 407, 1930), it has been suggested that the oxidation is the resultant of three consecutive processes:—

- (a) The condensation of oxygen at the oxide/oxygen interface.
- (b) The evaporation of the oxygen into the oxide.
- (c) The diffusion of oxygen through the oxide.

On this basis it has been possible to interpret the kinetics of the oxidation during the initial stages at low pressures and

* Communicated by Prof. E. K. Rideal.

above the limiting pressure. It is the purpose of this paper to attempt to extend the range of the quantitative treatment of the reaction kinetics by considering the oxidation when the oxide/oxygen interface is not saturated, but is yet in equilibrium with the gas phase.

For the rate of condensation we may write

$$kfp(1-\theta), \dots \dots \dots (1)$$

where θ is the fraction of the oxide surface covered with adsorbed oxygen at pressure p and f is the accommodation coefficient:

For the rate of evaporation we have,

$$(v_s + v_g)\theta + vp\theta, \dots \dots \dots (2)$$

where v_s and v_g are the rates of evaporation into the oxide and gas phase, respectively, and v is the rate of evaporation caused by impacts between free and adsorbed molecules. Since it has been shown (see P. R. S. above) that initially and at low pressure no adsorption equilibrium exists at the oxide/oxygen interface, we may not in the general case equate (1) and (2), for we must consider the gradual building up of the adsorption layer to a value θ , at which equilibrium is reached. The rate of growth θ is therefore given by

$$d\theta/dt = kfp(1-\theta) - (v_s + v_g)\theta - vp\theta \dots \dots (3)$$

This may be written, for simplicity, as

$$d\theta/dt = k_2p(1-k_1\theta) - k_3\theta, \dots \dots \dots (4)$$

where k_1 , k_2 , and k_3 are constants.

Considering, now, the diffusion process, we may, since adsorption appears to be a necessary preliminary to diffusion, write the rate of diffusion as

$$k\theta/p_0 - p.$$

The rate of fall of pressure of oxygen is governed by the rate of sorption by the oxide and the rate of diffusion through the oxide layer. Since sorption and adsorption are closely related, we may write the rate of sorption as proportional to the rate of adsorption $d\theta/dt$.

We have, therefore, for the total rate of change of pressure

$$-dp/dt = k_4d\theta/dt + k\theta/p_0 - p; \dots \dots (6)$$

$k_4 d\theta/dt$ may be termed, shortly, the rate of sorption of oxygen.

Eliminating θ and $d\theta/dt$ from (4) and (6) we find

$$dp/dt = \frac{k_4(dp/dt + k)(dp/dt + k_2p) - (p_0 - p)(d^2p/dt^2 + k_2dp/dt)}{k - k_4(p_0 - p)(k_2k_1p + k_3)} \\ + \frac{k_4^2 dp/dt(p_0 - p)(dp/dt + k_2p)[k_2k_1(p_0 - p) - (k_2k_1p + k_3)]}{[k - k_4(p_0 - p)(k_2k_1p + k_3)]^2}.$$

This equation is the general equation describing the kinetics of the reaction. It has been found to be much too complicated to apply to the experimental results.

Simplified forms of the equations are, however, readily obtained. In the first place it is necessary to show that, under the appropriate conditions, the logarithmic equation for the initial oxidation* and the parabolic equation are obtained.

Under the conditions of the initial oxidation at low pressures $\theta = 0$, and (4) and (6) become

$$k_2p = d\theta/dt$$

$$-dp/dt = k_4d\theta/dt,$$

and therefore

$$-dp/dt = k_4k_2p.$$

When the oxidation follows the parabolic law, the surface is saturated, and therefore $\theta = 1/k_1$ and $d\theta/dt = 0$. Therefore

$$-dp/dt = \frac{k/k_1}{(p_0 - p)}.$$

A very interesting case is obtained if we consider the slightly more complicated problem in which the oxide has reached † adsorption and absorption equilibria. It is clear that even when the pressure is below the limiting pressure a sorption equilibrium will be established after a definite time, and $d\theta/dt$ will be zero.

Under these conditions (4) and (6) become

$$k_2p(1 - k_1\theta) - k_3\theta = 0 \quad . \quad . \quad . \quad (7)$$

$$-dp/dt = k\theta/p_0 - p. \quad . \quad . \quad (8)$$

Substituting for θ in (8), we get

$$-dp/dt = \frac{k k_2 p}{(p_0 - p)(k_1 k_2 p + k_3)} \quad . \quad . \quad . \quad (9)$$

* See Proc. Roy. Soc. above.

† The adsorption and absorption equilibria will be referred to henceforward as a sorption equilibrium.

This equation on integration gives, with suitable rearrangement of terms, the linear equation

$$t/(p_0-p)^2 = \frac{\alpha[p_0(\log_e p_0/p-1)+p]}{(p_0-p)^2} + \beta, \quad (10)$$

where α and β are constants equal to k_3/kk_2 and $k_1/2k$ respectively.

It is clear that under the conditions of surface saturation (10) reduces to the parabolic equation; for, from (5), we see that the condition for surface saturation is that $p \gg k_3/k_1k_2$: when this holds

$$\beta \gg \frac{\alpha[p_0(\log_e p_0/p-1)+p]}{(p_0-p)^2}$$

and (10) becomes

$$t/(p_0-p)^2 = \beta.$$

This result is, however, no test of the validity of (10), since the initial assumptions were made of such a nature as to give it. We may, however, note that the parabolic law is only valid when a surface equilibrium has been obtained. The experiments described in another place (see P. R. S. above) together with those of Dunn (Proc. Roy. Soc. A, cxi. p. 210, 1926) would appear to show that when the pressure is above limiting pressure, this equilibrium is attained before the first one or two readings are taken, that is, within about 100 sec. Evans and Bannister (Proc. Roy. Soc. A, cxxv. p. 370, 1929) have shown that the attack of silver by iodine in solution in chloroform is less rapid than is expected from the parabolic law. Since sorption equilibria are attained in general less rapidly at a liquid-gas than at a solid-gas interface, one might interpret this deviation from the parabolic law to the circumstance that a sorption equilibrium was not established between the solid and the solution while the first few readings were being taken.

Oxidation below the Limiting Pressure: the Establishment of Sorption Equilibria.

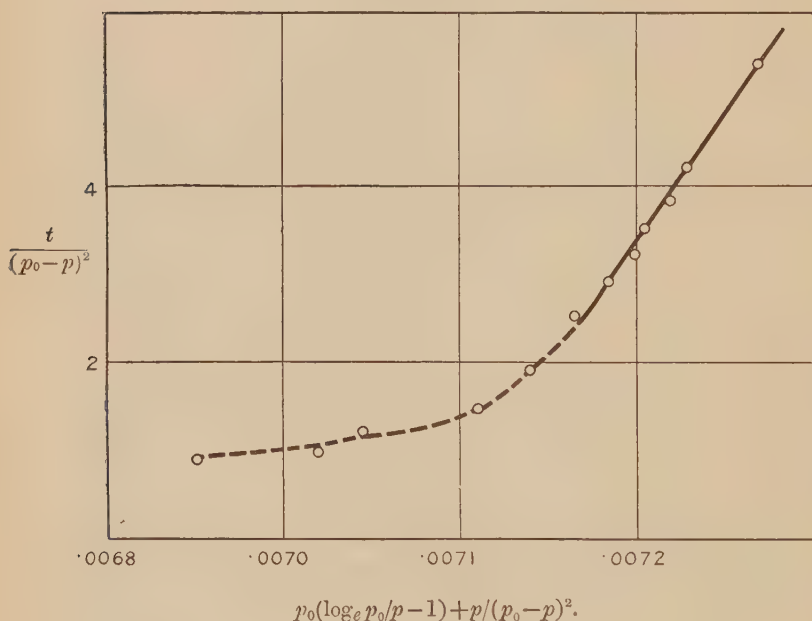
In order to test the validity of the equation

$$t/p_0-p)^2 = \frac{\alpha[p_0(\log_e p_0/p-1)] + p}{(p_0-p)^2} + \beta. \quad (10)$$

it is necessary to apply it to experiments under such conditions that the correcting term to the parabolic equation, $\frac{\alpha[p_0(\log_e p_0/p-1)+p]}{(p_0-p)^2}$ takes on finite values. Owing to the

fact that the saturation values at a surface are approached asymptotically as p is increased, it is clear that in the neighbourhood of the limiting pressure the correcting term will always be small. Experiments for the testing of (10) were therefore carried out at pressures below the limiting pressure. The earlier discussion entered into, however, shows that in such experiments it is possible that a finite time will be required to establish the sorption equilibria. It is to be expected, therefore, that (10) will be invalid over the earlier

Fig. 1.



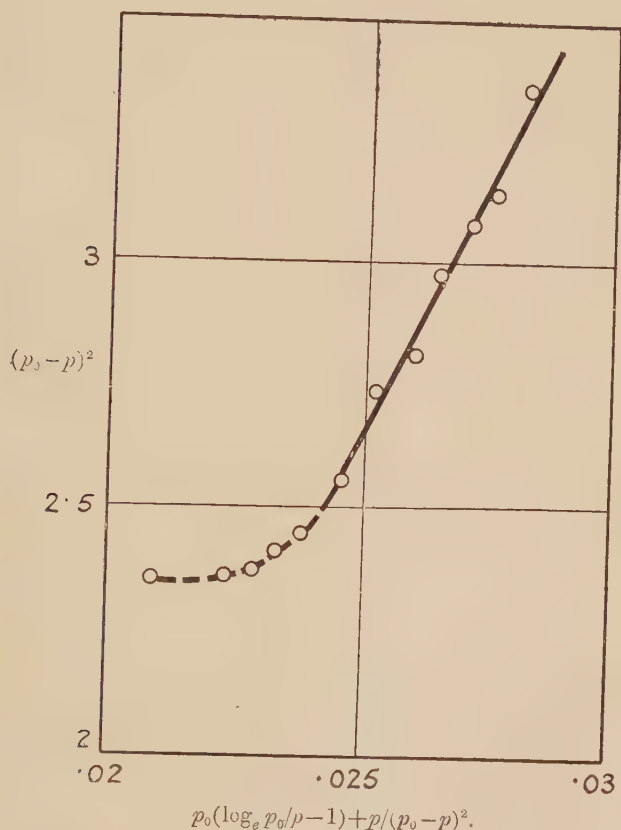
stages of the oxidation, although it ought to describe the progress of the oxidation in the later stages accurately. Experiment has verified these predictions completely.

From a series of experiments below the limiting pressure, the values of $t/(p_0 - p)^2$ and $\frac{p_0(\log_e p_0/p - 1) + p}{(p_0 - p)^2}$ were calculated and plotted. Three examples of the curves so obtained are given in figs. 1-3. The corresponding experimental data are tabulated in Tables I.-III.

The curves show that, after an initial deviation, the curves are strictly linear: that is, as predicted, equation (10) is valid only over the later stages of the oxidation.

Accepting now that the initial deviation from linearity in figs. 1-3 is due to the circumstance that a sorption equilibrium

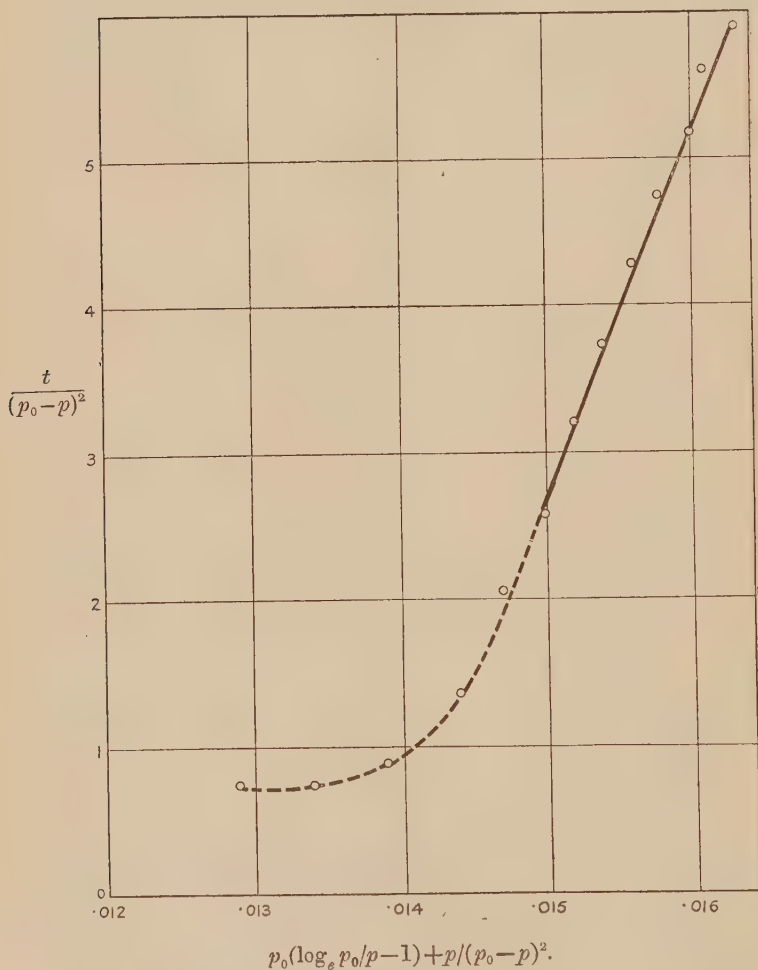
Fig. 2.



is not established until the oxidation had been proceeding for a finite time, we may proceed further and determine the times at which (10) first becomes linear. Clearly these times will represent the time t_c required to establish the equilibrium. The values of t_c obtained from the three illustrative experiments are 609, 533, and 185 sec. respectively. Owing to the wide differences in these values, a series of

experiments was carried out in order to see how far t was dependent upon the state of activation of the surface.

Fig. 3.



The figures obtained are collected in Table IV. The extent of activation is measured by the number of times the copper has been oxidized and reduced.

TABLE I.

t in secs.	p in mm.	$t/(p_0-p)^2$.	$\frac{p_0(\log_e p_0/p-1)+p}{(p_0-p)^2}$.
27	73.04	—	—
56	70.14	.879	.00690
79	68.89	.927	.00704
141	67.17	1.18	.00709
186	66.64	1.41	.00721
246	65.85	1.53	.00717
300	65.44	1.87	.00728
480	64.29	2.51	.00733
607	63.57	2.87	.00737
720	63.10	3.19	.00740
840	62.61	3.50	.00741
960	62.31	3.84	.00744
1142	61.63	4.20	.00746
1520	61.28	5.38	.00754

TABLE II.

t in secs.	p in mm.	$t/(p_0-p)^2$.	$\frac{p_0(\log_e p_0/p-1)+p}{(p_0-p)^2}$.
36	36.47	.750	.0129
59	34.54	.752	.0134
98	32.95	.897	.0138
149	31.82	1.11	.0138
211	30.99	1.37	.0144
383	29.75	2.06	.0147
533	29.02	2.58	.0150
743	28.18	3.21	.0152
923	27.69	3.74	.0154
1133	27.13	4.28	.0156
1343	26.61	4.76	.0158
1553	26.08	5.18	.0160
1763	25.68	5.61	.0161
1943	23.25	5.90	.0163

TABLE III.

t in secs.	p in mm.	$t/(p_0-p)^2$.	$\frac{p_0(\log_e p_0/p - 1) + p}{(p_0 - p)^2}$.
26	22.88	2.36	.0209
66	20.92	2.368	.0224
91	20.01	2.374	.0228
112	19.40	2.42	.0233
139	18.67	2.45	.0238
185	17.70	2.56	.0246
228	17.08	2.74	.0251
282	16.19	2.82	.0260
329	15.70	2.98	.0265
373	15.19	3.08	.0271
415	14.71	3.14	.0276
488	14.15	3.36	.0282

The Influence of Activation on t_c .

TABLE IV.

No. of expt.	No. of oxidations and reductions.	t_c in sec.
9a.....	16	500
10a.....	17	600
11a.....	18	700
12a.....	19	700
13a.....	20	750
15a.....	24	800

The reductions before 9a were carried out at 305° C., and afterwards at 183° C. It would appear, therefore, that three or four oxidations and reductions at 183° are required to bring a surface into a steady state of activation after previous activation at 305°*.

The results of a second set of experiments are given in Table V.:

TABLE V.

No. of expt.	No. of oxidations and reductions.	t_c in sec.
2c.....	1	180
4c.....	4	200
6c.....	6	400

The reductions between 4c and 6c were at 183°.

* Cf. Dunn, Proc. Roy. Soc. A, cxi. p. 210 (1926).

The results clearly show that activation increases t_c . If we consider (3) the reason is obvious

$$kfp(1-\theta)-(v_s+v_g)\theta-vp\theta=d\theta/dt \quad . \quad . \quad . \quad (3)$$

The value of t_c is dependent upon $d\theta/dt$. If $d\theta/dt$ is small, t_c is large and *vice versa*. Now (3) shows that the larger v_s is the smaller is $d\theta/dt$. The earlier study (*loc. cit.*) of the limiting pressure gives good ground for believing that v_s increases with activation, and, therefore, t_c should also increase with activation. This work on the influence of activation on t_c , therefore, brings a third piece of evidence in favour of the view that the oxygen adsorbed on cuprous oxide is able to diffuse laterally. In conclusion, it is of interest to note that with the exception of the evidence obtained by Germer (*Zeits. f. Phys.* liv. p. 408, 1929) in his work on the influence of the adsorbed gas on the diffraction of electrons by a surface, all the evidence for lateral diffusion has been obtained from experiments with vapours [*e. g.* see Volmer, *Z. Physik*, ix. p. 193 (1922); Moll, *Z. phys. Chem.* cxxxviii. p. 183 (1928); Cockcroft, Roy. Soc. Proc. cxix. p. 294 (1928)].

Further, it may be pointed out that the concept of the adsorbed gas layer developed in this research is also not without interest in connexion with the theory of catalysis developed by Pietsch and Schwab (*Z. p. Chem.* B, i. p. 385, 1929), particularly when it is remembered that it has been suggested that increase in activation of a copper surface is accompanied by decrease in the grain size, and therefore increase in the extent of grain boundary.

Summary.

The general kinetic equations are developed for the oxidation of copper in a closed system. The most general equation is too complicated to be applied to the experimental results. A slightly simpler case is dealt with in which it is assumed that a sorption equilibrium exists between the oxide film and the gas phase. The equation obtained is found to provide an accurate description of the results under the requisite conditions. Further, it is shown that the time taken for a sorption equilibrium to be established increases with the activation of the surface. This result finds a ready interpretation if it is assumed that the adsorbed oxygen is able to diffuse laterally.

The results are considered in their relation to the theory of adsorption at the gas/solid interface and catalysis.

My thanks are due to Prof. E. K. Rideal for his continued interest and advice during the course of this research, and to the British Non-Ferrous Metals Research Association for a grant.

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XXXIII. *On Heaviside's Operational Solution of a Volterra's Integral Equation when its Nucleus is a Function of $(x-\xi)$.*
By S. KOIZUMI*.

1. *Heaviside's Operational Solution of a Volterra's Integral Equation.*

LET us consider the following integral equation

$$f(x) = C \psi(x) + \int_0^x \psi(\xi) K(x-\xi) d\xi \quad . \quad . \quad (1)$$

where $f(x)$ is a given function and C is a parameter. This is a Volterra's integral equation of the second kind with the special nucleus. In the case $C = 0$, it becomes a Volterra's integral equation of the first kind.

To solve the integral equation (1) operationally, multiply throughout with e^{-px} , and integrate between zero and infinity, as van der Pol proceeded to solve the linear differential equation operationally†.

Then

$$\begin{aligned} \int_0^\infty e^{-px} f(x) dx &= C \int_0^\infty e^{-px} \psi(x) dx \\ &+ \int_0^\infty e^{-px} dx \int_0^x \psi(\xi) K(x-\xi) d\xi \quad . \quad . \quad . \quad (2) \end{aligned}$$

By virtue of Dirichlet's formula, if $\psi(\xi) K(x-\xi)$ is a continuous function of both variables; the last integral of the right side of (2) will be transformed as follows:—

* Communicated by the Author.

† Balth. van der Pol, Phil. Mag. vii. p. 1153 (1929), and viii. p. 861 (1929).

$$\left. \begin{aligned} \int_0^\infty e^{-px} dx \int_0^x \psi(\xi) K(x-\xi) d\xi \\ = \int_0^\infty \psi(\xi) d\xi \int_\xi^\infty e^{-px} K(x-\xi) dx \\ = \int_0^\infty e^{-p\xi} \psi(\xi) d\xi \int_0^\infty e^{-p\eta} K(\eta) d\eta \end{aligned} \right\} \quad . \quad . \quad (3)$$

Thus

$$\int_0^\infty e^{-px} \psi(x) dx = \int_0^\infty e^{-px} f(x) dx \left/ \left(C + \int_0^\infty e^{-px} K(x) dx \right) \right. \quad (4)$$

If we put

$$\left. \begin{aligned} p \int_0^\infty e^{-px} \psi(x) dx &= \Phi(p) \\ p \int_0^\infty e^{-px} f(x) dx &= F(p) \\ p \int_0^\infty e^{-px} K(x) dx &= N(p) \end{aligned} \right\} \quad . \quad . \quad . \quad (5)$$

(4) becomes

$$\Phi(p) = F(p) \left/ \left(C + \frac{N(p)}{p} \right) \right. \quad . \quad . \quad . \quad (6)$$

The functions $\Phi(p)$, $F(p)$, and $N(p)$ defined by (5) are called the operational expression of $\psi(x)$, $f(x)$, and $K(x)$ respectively, and this relation will be denoted henceforth by a symbol \doteq in the following manner*:

$$\Phi(p) \doteq \psi(x) \quad \text{or} \quad \psi(x) \doteq \Phi(p) \text{ etc.}$$

Thus if we can find the function $\psi(x)$ which satisfies the relation

$$\psi(x) \doteq F(p) \left/ \left(C + \frac{N(p)}{p} \right) \right. \quad . \quad . \quad . \quad (7)$$

this will be the solution of the integral equation (1).

It was established first by Bromwich that when the operational expression $H(p)$ of the unknown function $h(x)$ is given, the latter is expressed by the following complex integral:

$$h(x) = \frac{1}{2\pi i} \int_{l-i\infty}^{l+i\infty} e^{px} \frac{H(p)}{p} dp,$$

* Balth. van der Pol uses the symbol \doteq (Phil. Mag. viii. p. 863, 1929).

where l is a positive and finite constant such that all singularities of the integrand are on the left side of the line which is parallel to the imaginary axis and distant l from it. The result of the evaluation of the above complex integral is the same as Heaviside's operational treatment of $H(p)$.

The solution of the integral equation (1), therefore, will be given by the complex integral

$$\psi(x) = \frac{1}{2\pi i} \int_{l-i\infty}^{l+i\infty} e^{px} \frac{F(p)}{Cp + N(p)} dp \quad \dots \quad (8)$$

or by the operational treatment of (7) considering

$$p^{-n} \doteq x^n / \Gamma(1+n).$$

Thus Heaviside's operational calculus, which has been adopted hitherto chiefly to solve differential equations, will be applicable also to the integral equation of the above type.

Using the above notation the relation (3) will be written down as follows :

$$\int_0^x \psi(\xi) K(x-\xi) d\xi \doteq \frac{\Phi(p) \cdot N(p)}{p} \quad \dots \quad (9)$$

In the case $K(x) = 1$, (9) becomes

$$\int_0^x \psi(\xi) d\xi \doteq \frac{\Phi(p)}{p} \quad \dots \quad (10)$$

As it is obtainable at once from the definition of the operational expression that when $h(x) \doteq H(p)$ then

$$\frac{dh(x)}{dx} \doteq pH(p) - h(0)p \quad \dots \quad (11)$$

we have from (9)

$$\frac{d}{dx} \int_0^x \psi(\xi) K(x-\xi) d\xi \doteq \Phi(p) \cdot N(p). \quad \dots \quad (12)$$

Thus when it is possible to write

$$F(p) \left/ \left(C + \frac{N(p)}{p} \right) \right. = F_1(p) F_2(p),$$

and if the functions $f_1(x)$ and $f_2(x)$ are known which are defined by the equations

$$F_1(p) \doteq f_1(x) \quad F_2(p) \doteq f_2(x),$$

then by (12) the explicit expression of (6) will be written in the following form :

$$\psi(x) = \frac{d}{dx} \int_0^x f_1(\xi) f_2(x-\xi) d\xi. \quad . \quad . \quad (13)$$

or

$$\psi(x) = f_2(0) f_1(x) + \int_0^x f_1(\xi) f_2'(x-\xi) d\xi. \quad . \quad (14)$$

Example 1.—Abel's integral equation

$$f(x) = \int_0^x \frac{\psi(\xi)}{(x-\xi)^\mu} d\xi, \quad 0 < \mu < 1.$$

Solution :

As

$$K(x) = x^{-\mu} = \frac{\Gamma(1-\mu)}{p^{-\mu}} = N(p),$$

by (6)

$$\Phi(p) = F(p)/\Gamma(1-\mu)p^{\mu-1}.$$

But

$$\frac{1}{\Gamma(1-\mu)p^{\mu-1}} = \frac{1}{\Gamma(1-\mu)\Gamma(\mu)x^{1-\mu}} = \frac{\sin \mu\pi}{\pi} \frac{1}{x^{1-\mu}}.$$

Hence by (13)

$$\psi(x) = \frac{\sin \mu\pi}{\pi} \frac{d}{dx} \int_0^x f(\xi) \frac{d\xi}{(x-\xi)^{1-\mu}}.$$

Example 2.—

$$f(x) = \psi(x) + \int_0^x \psi(\xi) \frac{1}{\sqrt{x-\xi}} d\xi.$$

Solution :

$$K(x) = x^{-\frac{1}{2}} = (\pi p)^{\frac{1}{2}} = N(p),$$

$$\therefore \Phi(p) = F(p) \left\{ 1 + \left(\frac{\pi}{p} \right)^{\frac{1}{2}} \right\}.$$

But

$$\begin{aligned} \frac{1}{1 + \left(\frac{\pi}{p} \right)^{\frac{1}{2}}} &= e^{\pi x} \left(1 - \int_0^x \frac{e^{-\pi \lambda}}{\sqrt{\lambda}} d\lambda \right) \\ &= e^{\pi x} (1 - \text{Erf}(\sqrt{\pi x})) = h(x). \end{aligned}$$

Hence

$$\psi(x) = \frac{d}{dx} \int_0^x f(\xi) h(x-\xi) d\xi.$$

Example 3.—

$$f(x) = \int_0^x \psi(\xi) \cos(x-\xi) d\xi.$$

Solution :

$$K(x) = \cos x \doteq \frac{p^2}{p^2+1} = N(p),$$

$$\therefore \psi(x) \doteq F(p) \cdot \frac{p^2+1}{p}.$$

If $f(x) = \sin x$, i. e.,

$$F(p) = \frac{p}{p^2+1},$$

then

$$\psi(x) = 1.$$

If $f(x) = x$, i. e., $F(p) = p^{-1}$,

$$\begin{aligned} \psi(x) &\doteq \frac{1}{p} \cdot \frac{p^2+1}{p} = 1 + \frac{1}{p^2} \\ &= 1 + \frac{x^2}{2}. \end{aligned}$$

If

$$f(x) = 1,$$

then

$$\begin{aligned} \psi(x) &\doteq \frac{1}{p} + p \\ &= x + \delta(x), \end{aligned}$$

where $\delta(x)$ is Dirac's function *. It has the property

$$\int_{-\infty}^{+\infty} f(x)\delta(x)dx = f'(0),$$

and it is zero everywhere except at $x = 0$, where it is infinite.

2. The Operational Expression of the Reciprocal Function.

When C is not equal to zero, the equation (1) will be written in the following form :

$$f(x) = \psi(x) - \lambda \int_0^x \psi(\xi) K(x-\xi)d\xi. \quad . \quad . \quad (15)$$

If we put

$$R(p) = -N(p) \left/ \left(1 - \frac{\lambda N(p)}{p} \right) \right. \quad . \quad . \quad . \quad (16)$$

* Cf. Balth. van der Pol, Phil. Mag. viii. p. 865 (1929).

the equation (6) will be written as follows :

$$\Phi(p) = F(p) - \lambda \frac{F(p) R(p)}{p}.$$

Or by (9)

$$\psi(x) = f(x) - \lambda \int_0^x f(\xi) L(x-\xi) d\xi. \quad \dots (17)$$

where $L(x-\xi)$ is the reciprocal function of $K(x-\xi)$ and is defined by the equation

$$L(x) \doteq R(p) \quad \dots \dots \dots (18)$$

Example.—

$$f(x) = \psi(x) - \lambda \int_0^x \psi(\xi) \sin(x-\xi) d\xi.$$

Solution :

As

$$K(x) = \sin x \doteq \frac{p}{p^2+1} = N(p)$$

by (16)

$$R(p) = \frac{-p}{p^2+(1-\lambda)}$$

Then by (18)

$$L(x) = -\frac{\sin(\sqrt{1-\lambda}x)}{\sqrt{1-\lambda}}.$$

Especially when $\lambda = 1$,

$$L(x) = -x.$$

3. *The Operational Solution of the Linear Differential Equation with Constant Coefficients.*

Let us consider the following differential equation :

$$a_n \frac{d^n y}{dx^n} + a_{n-1} \frac{d^{n-1} y}{dx^{n-1}} + \dots + ay = \gamma(x). \quad \dots (19)$$

To apply the above results to solve this equation, integrate both sides n -times repeatedly from zero to x . Then we shall obtain the following equation :

$$\begin{aligned} a_n y(x) + a_{n-1} \int_0^x y(x) dx + \dots + a \int_0^x \dots \int_0^x y dx^n \\ = \int_0^x \dots \int_0^x f(x) dx^n + A_1 \frac{x^{n-1}}{(n-1)!} + A_2 \frac{x^{n-2}}{(n-2)!} + \dots + A_n, \end{aligned} \quad \dots \dots (20)$$

where

$$\left. \begin{aligned} A_1 &= a_1 y(0) + a_2 y'(0) + \dots + a_n^{(n-1)} y(0) \\ A_2 &= a_2 y(0) + \dots + a_n^{(n-2)} y(0) \\ &\dots \dots \dots \\ A_n &= a_n y(0) \end{aligned} \right\} \dots (21)$$

As

$$\int_0^x \dots \int_0^x y(x) d\bar{x}^m = \int_0^x y(\xi) \frac{(x-\xi)^{m-1}}{(m-1)!} d\xi,$$

the equation (20) becomes

$$a_n y(x) + \int_0^x y(\xi) K^*(x-\xi) d\xi = f^*(x) \dots (22)$$

where

$$K^*(x) = a_{n-1} + a_{n-2} \frac{x}{1!} + a_{n-3} \frac{x^2}{2!} + \dots + a \frac{x^{n-1}}{(n-1)!},$$

and

$$f^*(x) = \int_0^x \dots \int_0^x f(x) d\bar{x}^n + A_1 \frac{x^{n-1}}{(n-1)!} + \dots + A_n.$$

Thus the differential equation (19) with its initial conditions is equivalent to the integral equation (22), which is the same type as we have considered in the foregoing articles.

Thus by (6)

$$\begin{aligned} \Phi(p) &= F^*(p) \left/ \left(a_n + \frac{N^*(p)}{p} \right) \right. \\ &= \frac{F(p) + A_1 p + A_2 p^2 + \dots + A_n p^n}{a_n p^n + a_{n-1} p^{n-1} + \dots + a} \dots (23) \end{aligned}$$

where

$$\Phi(p) \doteq y(x), \quad F^*(p) \doteq f^*(x), \quad N^*(p) \doteq K^*(x) \quad \text{and} \\ F(p) \doteq f(x).$$

Let

$$I(p) = (a_n p^n + a_{n-1} p^{n-1} + \dots + a)^{-1},$$

and its explicit equivalent be $\epsilon(x)$, then (23) becomes

$$\Phi(p) = F(p) I(p) + A_1 p I(p) + \dots + A_n p^n I(p).$$

Now since

$$\epsilon^{(\nu)}(0) \doteq \lim_{p \rightarrow \infty} p^\nu I(p) = 0, \quad \nu = 0, 1, \dots, n-1,$$

it follows from (11) and (12) that the explicit solution of (19) is

$$y(x) = \frac{d}{dx} \int_0^x f(\xi) \epsilon(x-\xi) d\xi \\ + A_1 \frac{d\epsilon}{dx} + A_2 \frac{d^2\epsilon}{dx^2} + \dots + A_n \frac{d^n\epsilon}{dx^n} \dots \quad (24)$$

4. *The Operational Solution of the Integro-Differential Equations.*

Let us consider the following integro-differential equation :

$$a_n \frac{d^n y}{dx^n} + a_{n-1} \frac{d^{n-1} y}{dx^{n-1}} + \dots + ay(x) \\ + \int_0^x y(\xi) K(x-\xi) d\xi = f(x). \quad \dots \quad (25)$$

If we integrate both sides n -times repeatedly from zero to x , the resultant form will be expressed operationally as follows :

$$\left(a_n + a_{n-1} \frac{1}{p} + \dots + a \frac{1}{p^n} + \frac{N(p)}{p^{n+1}} \right) \phi(p) \\ = \frac{F(p)}{p^n} + A_1 \frac{1}{p^{n-1}} + \dots + A_n,$$

where

$$\Phi(p) \doteq y(x), \quad F(p) \doteq f(x), \quad \text{and} \quad N(p) \doteq K(x),$$

and A_1, \dots, A_n are the same as (21).

Thus

$$y(x) = \frac{F(p) + A_1 p + A_2 p^2 + \dots + A_n p^n}{a_n p^n + a_{n-1} p^{n-1} + \dots + a + \frac{N(p)}{p}} \dots \quad (26)$$

In the same manner it will be possible to solve the more general integro-differential equation which follows.

$$\sum_{\nu=0}^n a_\nu \frac{d^\nu \psi(x)}{dx^\nu} + \sum_{\nu=0}^m \int_0^x \frac{d^\nu \psi(\xi)}{d\xi^\nu} K(x-\xi) d\xi = f(x) \quad (27)$$

5. *The Operational Solution of the System of Simultaneous Integral or Integro-Differential Equations.*

Now let us consider the following system of simultaneous integral equations :

$$\left. \begin{aligned} j_1(x) &= C_{11}\psi_1(x) + \int_0^x \psi_1(\xi) K_{11}(x-\xi) d\xi \\ &\quad + C_{12}\psi_2(x) + \int_0^x \psi_2(\xi) K_{12}(x-\xi) d\xi, \\ f_2(x) &= C_{21}\psi_1(x) + \int_0^x \psi_1(\xi) K_{21}(x-\xi) d\xi \\ &\quad + C_{22}\psi_2(x) + \int_0^x \psi_2(\xi) K_{22}(x-\xi) d\xi. \end{aligned} \right\} \dots (28)$$

This will be written down in the operational form,

$$\left. \begin{aligned} F_1(p) &= G_{11}(p)\Phi_1(p) + G_{12}(p)\Phi_2(p), \\ F_2(p) &= G_{21}(p)\Phi_1(p) + G_{22}(p)\Phi_2(p), \end{aligned} \right\} \dots (29)$$

provided that

$$\left\{ \begin{aligned} F_r(p) &\doteq f_r(x), \quad \Phi_r(p) \doteq \psi_r(x) \quad r = 1, 2, \\ G_{rs}(p) &\doteq C_{rs} + \int_0^x K_{rs}(x) dx \quad r, s = 1, 2. \end{aligned} \right\}$$

Thus

$$\left. \begin{aligned} \Phi_1(p) &= \left| \begin{array}{cc} F_1 & G_{12} \\ F_2 & G_{22} \end{array} \right| / \Delta \\ \Phi_2(p) &= \left| \begin{array}{cc} G_{11} & F_1 \\ G_{21} & F_2 \end{array} \right| / \Delta \end{aligned} \right\}, \dots (30)$$

where

$$\Delta = \left| \begin{array}{cc} G_{11}(p) & G_{12}(p) \\ G_{21}(p) & G_{22}(p) \end{array} \right|.$$

The equation (30) is the operational solution of the system of the simultaneous integral equation (28).

The present procedure will be also applicable to solve more complicated systems of simultaneous integral or integro-differential equations.

Summary.

In § 1 it is shown in the same manner as van der Pol proceeds to solve the linear differential equations operationally that Heaviside's operational calculus is applicable also to a Volterra's integral equation when its nucleus is a

function of $(x - \xi)$, and some examples such as Abel's integral equation are treated operationally.

In § 2 the operational expression of the reciprocal function is considered.

In § 3, § 4, and § 5 the operational solutions of differential equations and integro-differential equations are considered.

Although the integral equation treated here is a special case of Volterra's integral equation, its operational treatment will be very useful in the problem of electric circuit theory.

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Tokyo, April 1930.

XXXIV. *An Extension of Ramsay and Young's Boiling-point Rule.* By T. S. WHEELER*, Ph.D., F.R.C.Sc.I., F.I.C.

INTRODUCTION.

DÜHRING⁽¹⁾ found that the absolute temperatures for which a pair of liquids have equal vapour pressures are connected by an approximately linear equation. Ramsay and Young⁽²⁾ discovered a more accurate relation between the temperatures of equal vapour pressures of two liquids. It is

$$\frac{T_{1p}}{T_{2p}} = \frac{T_{1p'}}{T_{2p'}} + c(T_{1p} - T_{1p'})$$

(c is a constant; $T_{1p'}$ and $T_{2p'}$ are the absolute temperatures at which the liquids 1 and 2 have a given vapour pressure p'), which is linear in $\frac{1}{T_{1p}}$ and $\frac{1}{T_{2p}}$ ^{(3) (4)}.

Cox⁽⁵⁾ pointed out that the reciprocals of the absolute temperatures of equal vapour pressures of two liquids satisfy an equation of the first degree, apparently without realizing that this relation is implied in Ramsay and Young's rule.

In the present paper it is shown that this rule is a special case of a more general relation, applicable both to single liquids and to pairs of liquids, which may be called "the

* Communicated by Prof. F. G. Donnan, F.R.S.

reciprocal temperature rule." This new rule can be stated thus :—

The reciprocals of the absolute temperatures, for which two given powers of the vapour pressures of a liquid or of a pair of liquids are in a constant ratio, satisfy a linear equation.

This rule need not be limited to liquid-vapour systems, but can be referred to any system to which the integrated form of the van't Hoff isochore is applicable.

It has also been found that Dühring's rule is a special case of a more general rule.

THE RECIPROCAL TEMPERATURE RULE FOR SINGLE LIQUIDS.

We assume that the vapour-pressure temperature curve of a liquid can be expressed in the form

$$f(p) = a + b/T_p \quad . \quad . \quad . \quad . \quad . \quad (1)$$

(a and b are constants), and that for two particular values of the vapour pressure, p_1 and p_2 , we have

$$f(p_1) = a + b/T_{p_1} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

and

$$f(p_2) = a + b/T_{p_2} \quad . \quad . \quad . \quad . \quad . \quad (3)$$

If T_{p_1} and T_{p_2} are chosen so that

$$p_1 = mp_2^n$$

(m and n are constants), we have from (2)

$$f(mp_2^n) = a + b/T_{p_1} \quad . \quad . \quad . \quad . \quad . \quad (4)$$

If $f(p)$ is of such a form that

$$f(mp^n) = k_1 + k_2 f(p) \quad . \quad . \quad . \quad . \quad . \quad (5)$$

(k_1 and k_2 are constants), then from (3), (4), and (5),

$$a + b/T_{p_1} = k_1 + k_2(a + b/T_{p_2}), \quad . \quad . \quad . \quad . \quad . \quad (6)$$

which is an equation of the first degree in

$$1/T_{p_1} \quad \text{and} \quad 1/T_{p_2}.$$

Now (5) is satisfied if

$$f(p) = \log p,$$

and Rankine's simplified equation

$$\log p = a + b/T_p \quad . \quad . \quad . \quad . \quad . \quad (7)$$

holds with fair accuracy for many liquids over limited ranges of temperature; hence we can deduce that, within the limits of validity of (7),

(A) *The reciprocals of the absolute temperatures, for which two given powers of the vapour pressures of a liquid are in a constant ratio, satisfy a linear equation.*

(A) may be called the "reciprocal temperature rule for single liquids."

For the particular case for which in (5)

$$n=1$$

a second solution to (5) is provided by

$$f(p) = p^q$$

(q is a constant).

Now Bertrand's equation⁽⁴⁾

$$p^q = a + b/T_p, \quad \dots \dots \dots (8)$$

which can be deduced from thermodynamical principles, is an accurate expression for representing the vapour pressures of many substances over wide ranges of temperature. Hence we may expect (A) to hold with considerable accuracy when restricted to temperatures for which the vapour pressures of a liquid are in a constant ratio.

THE RECIPROCAL TEMPERATURE RULE FOR PAIRS OF LIQUIDS.

Assuming that the vapour-pressure curves of two liquids can be expressed by the equations

$$f(p) = a_1 + b_1/T_{1p} \quad \dots \dots \dots (9)$$

and

$$f(p) = a_2 + b_2/T_{2p} \quad \dots \dots \dots (10)$$

(a_1, a_2, b_1, b_2 are constants), we can deduce the reciprocal temperature rule for pairs of liquids to which (7) applies by the method used with a single liquid. The rule is:

(B) *The reciprocals of the absolute temperatures, for which two given powers of the vapour pressures of a pair of liquids are in a constant ratio, satisfy a linear equation.*

Bertrand's equation (8), using a constant value of q ($=0.02$), applies to many liquids with accuracy over wide ranges of temperature. Hence, as before, we may expect (B) to hold with considerable accuracy when restricted to

temperatures for which the vapour pressures of two liquids are in a constant ratio.

In the special case of temperatures of equal vapour pressures (B) reduces to Ramsay and Young's rule. For this to be true it is only necessary that (9) and (10) hold; there is no restriction of the form of $f(p)$, provided it is the same for both liquids⁽⁴⁾.

SOME DEDUCTIONS FROM THE GENERAL RULE.

Combining (A) and (B), and making use of the fact that if two variables stand in linear relationship with a third they are themselves linearly related, we can readily deduce:

(a) If the reciprocals of the absolute temperatures of equal vapour pressure of a standard liquid to which (A) applies, *e. g.*, water, and of any given liquid, satisfy a linear equation, then (B) applies as regards the liquid and water and (A) applies to the given liquid.

It is also clear that:

(b) If (B) holds as regards two liquids each with a third, then it also holds for the two liquids. Hence:

(c) (A) and (B) apply to any liquids for which, in conjunction with a standard liquid to which (A) applies, Ramsay and Young's rule has been established.

A large number of liquids are thus brought within the scope of (A) and (B), apart from any information as to the vapour pressure-temperature equations.

SOME TESTS OF THE ABOVE CONCLUSIONS.

The application of (A) to water, mercury, sulphur, hydrogen, and acetic acid has been tested, using the range of data given in the International Critical Tables. The method used was to plot $1/T_p$ against $1/T_{p/2}$ and against $1/T_{p/10}$; the fact that straight lines were obtained showed that (A) was true not only for ratios of 2 to 1 and 10 to 1, but also for the ratio of 5 to 1; ratios of up to 1000 to 1 were covered in this way. $1/T_p$ was also plotted against $1/T_{\sqrt{p}}$ and $1/T_{\sqrt[3]{p}}$; here again use was made of the fact that if (A) applies as regards $1/T$ and, respectively, $1/T_{p_1}$ and $1/T_{p_2}$, where $p = m p_1^n = m_1 p_2^{n_1}$, then it applies as regards $1/T_{p_1}$ and $1/T_{p_2}$.

The rule for pairs of liquids has been tested for water and acetic acid, mercury, helium, iodine, carbon disulphide, hydrogen, oxygen, benzene, and fluoro-benzene for vapour

pressures in the ratio of the critical pressures, so that comparisons could be made up to the critical points, and also for ratios of some powers of the vapour pressures. The only anomaly observed occurs with helium below about 3° K. Keesom and Wolkfe⁽⁶⁾ have shown that at a pressure of about 38 mm. (2·3° K.) a peculiar change occurs in liquid helium: there appear to be two liquid states. This may perhaps account for the anomaly.

The reciprocal temperature rule has also been found to apply to some two-component systems, *e. g.*, to aqueous solutions of sodium hydroxide containing more than 50 per cent. of water, and to unsaturated solutions of sodium chloride and sodium sulphate. The rule is also applicable, for the relatively restricted range for which data are available, to the partial pressures of water and anhydrous acid vapour over aqueous solutions of hydrogen chloride and of sulphuric acid, and to the total pressures of these solutions.

UTILITY OF THE RECIPROCAL TEMPERATURE RULE.

This rule can obviously be used to interpolate and extrapolate vapour-pressure temperature curves. By means of (A), for example, we can use one portion of a vapour-pressure curve to determine another by plotting $1/T_p$ against $1/T_{mp}$ up to T_{mp} corresponding to the highest given pressure, producing the straight line so obtained, and using T_{mp} to determine T_{m^2p} , and so on.

If (B) is employed for interpolation and extrapolation purposes, then, by choosing suitable values for m and n in the relation

$$p_1 = mp_2^n,$$

it is possible to use a standard liquid such as water in conjunction with a liquid with a much greater range of vapour pressure, such as mercury.

Thus, by plotting reciprocal temperatures for the relation

$$p_{\text{H}_2\text{O}} = \sqrt[3]{p_{\text{Hg}} \times 10^7}$$

(p in mm. of mercury), it is possible to compare the whole known vapour-pressure range of mercury ($1\cdot24 \times 10^{-6}$ mm. at -39°C. to 635,300 mm. at 1300°) with that of water. The rule has been tested and found to hold for this relation.

Further, if the equation to the vapour-pressure temperature curve of the standard liquid is known in the form

$$f(p) = a + b/T_{1p},$$

then the determination of the equation to the line obtained by plotting $1/T_{1p_1}$ for the standard liquid against $1/T_{2p_2}$ for a given liquid, where

$$p_1 = mp_2^n,$$

enables an equation to the vapour-pressure temperature curve of the given liquid to be at once deduced.

ALTERNATIVE METHOD OF STATING THE RECIPROCAL TEMPERATURE RULE.

Since the reciprocal temperature rule can be stated in the form

$$A/T_{p_1} + B/T_{p_2} = 1 \quad . \quad . \quad . \quad . \quad (11)$$

or

$$A/T_{1p_1} + B/T_{2p_2} = 1, \quad . \quad . \quad . \quad . \quad (12)$$

according as one or two liquids are involved, it follows that it may be stated⁽⁷⁾:

(C) *If the absolute temperatures for which two given powers of the vapour pressures of a liquid or of a pair of liquids are in a constant ratio are represented by lengths OX, OY laid off along two lines inclined at any angle, the line XY joining these extremities will, when produced, pass through a fixed point.*

APPLICATION OF THE RECIPROCAL TEMPERATURE RULE TO THE CALCULATION OF LATENT HEATS OF VAPORIZATION.

Under conditions for which the simplified Clausius-Clapeyron equation is valid we may write for limited ranges of temperature

$$\ln p = a_1 - L_1/RT_{1p} \quad . \quad . \quad . \quad . \quad (13)$$

and

$$\ln p = a_2 - L_2/RT_{2p} \quad . \quad . \quad . \quad . \quad (14)$$

(L_1, L_2 are the latent heats of liquids 1 and 2 respectively); whence, if

$$p_1 = mp_2^n,$$

$$a_1 - L_1/RT_{1p_1} = \ln m + na_2 - nL_2/RT_{2p_2}, \quad . \quad . \quad (15)$$

so that the slope of the reciprocal temperature line for pairs of liquids, provided (13) and (14) are valid, enables the ratio of the latent heats to be calculated.

If $T_{1p_1'}$ and $T_{2p_2'}$ are two other corresponding temperatures we have

$$\frac{L_1}{L_2} = \frac{n(1/T_{2p_2} - 1/T_{2p_2'})^{(8)}}{(1/T_{1p_1} - 1/T_{1p_1'})} \quad . \quad . \quad . \quad (16)$$

APPLICATION OF THE RECIPROCAL TEMPERATURE RULE TO SYSTEMS IN GENERAL.

It will be clear that any equilibrium system to which an equation of the form

$$\log (\text{variable}) = a + b/T$$

can be applied falls within the scope of the reciprocal temperature rule; for example, the reciprocals of the absolute temperatures for which the vapour pressures of water in mm. of mercury are numerically equal to K_p for the ammonia decomposition reaction at 10 atmospheres multiplied by 10^4 satisfy a linear equation.

The most general form of the reciprocal temperature rule can, accordingly, be stated thus:

- (D) *The reciprocals of the absolute temperatures, for which two given powers of a variable or pairs of variables which satisfy equations of the form $\log (\text{variable}) = a + b/T$ are in a constant ratio, satisfy a linear equation.*

The alternative form of statement given in (C) can also be employed.

This rule is of value, in that it enables a system which has been thoroughly studied to be applied to the interpolation and extrapolation of data relating to other systems. Thus, by applying graphically the reciprocal temperature rule to temperatures for which, say, the vapour pressures of water are ten times the vapour pressures of a substance as liquid and solid, the triple point of the substance is completely determined, as regards temperature and pressure, by the intersection of the two lines.

Alternatively, if the reciprocals of the temperatures of equal vapour pressure of a substance as liquid and solid are plotted, the point on the resulting straight line for which the variables have equal values corresponds to the triple point.

AN EXTENSION OF DÜHRING'S RULE.

The following extension of Dühring's rule has been found, empirically, to hold with fair accuracy over temperature ranges of the order of 100°C. —

- (E) *The absolute temperatures for which the vapour pressures of a liquid or of a pair of liquids are in a constant ratio satisfy a linear equation.*

This may be called "the absolute temperature rule." It

does not, in general, apply when powers of the vapour pressures are concerned.

We can reverse the argument used in establishing the reciprocal temperature rule, and deduce from (E) that, for liquids to which it applies, an equation of the form

$$p^q = a + bT$$

should hold over limited ranges of temperature.

By a process of trial and error it has been found that the equation

$$p^{5.7} = 0.188T_p - 3.83^*,$$

gives to within about 3° C. the temperature corresponding to any given vapour pressure of water up to about 1000 mm., and within about 6° C. up to the critical pressure.

OTHER VAPOUR PRESSURE EQUATIONS.

It is obvious that some other vapour-pressure temperature equations can be developed in the same manner as (1). Reference may be made to a modification of (7),

$$\log p = a + b/(T_p + c)^{(9)}$$

(a, b, c , are constants), from which rules involving $1/(T_p + c)$ can be deduced.

SUMMARY.

1. It is shown that Ramsay and Young's boiling-point rule is a special case of "the reciprocal temperature rule," which may be stated:—

The reciprocals of the absolute temperatures, for which two given powers of the vapour pressures of a liquid or a pair of liquids are in a constant ratio, satisfy a linear equation.

2. This rule can be stated in the following still more general form:—

The reciprocals of the absolute temperatures, for which two given powers of a variable or pair of variables which satisfy equations of the form $\log(\text{variable}) = a + b/T$ are in a constant ratio, satisfy a linear equation.

* It may be mentioned that the empirical equation

$$\log p = -2065/T_p^{1/150} + 8.17$$

gives, to within about 2° C., the absolute temperature corresponding to any given vapour pressure of water up to the critical point.

3. Dühring's rule may be regarded as a special case of "the absolute temperature rule" which holds with fair accuracy over temperature ranges of the order of 100°C. , and which may be stated:—

The absolute temperatures for which the vapour pressures of a liquid or of a pair of liquids are in a constant ratio, satisfy a linear equation.

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Sept. 1, 1930.

XXXV. *The Adsorption of Ions on a Surface Film.*

By R. S. BRADLEY*.

INCREASING attention has recently been paid to the effect of the supporting medium on a surface film. Thus Lyons and Rideal⁽¹⁾ have studied the changes in a surface film of insoluble fatty acid due to a changing p.h. of the underlying water. There is no doubt that we have here a diffuse ionic layer on the underside of the film.

In this paper the potential due to a uniform plane array of dipoles oriented perpendicular to the surface will be calculated. From this the magnitude of the adsorbed ionic layer can be computed. The problem is in fact the converse of that studied by Lennard-Jones and Dent⁽²⁾, the

* Communicated by the Author.

adsorption of molecules on the surface of an ionic crystal. In this paper only electrical forces will be considered.

The potential of an infinite sheet of uniformly spaced dipoles cannot be calculated directly, because then a series is obtained which converges too slowly. Instead the charges must be replaced by a Fourier development. Madelung⁽³⁾ has calculated in this way the potential due to a plane array of point charges of equal sign, and his result will be applied as follows.

The potential V due to a plane array of charges E , forming lines distances a and b apart, is given by

$$V = \frac{4E}{ab} \sum_{l=1}^{\infty} \sum_{m=1}^{\infty} \frac{e^{-2\pi(l^2 + \frac{m^2}{b^2})\frac{z}{a}}}{(l^2 + \frac{m^2}{b^2})^{\frac{1}{2}}} \cos \frac{2\pi lx}{a} \cos \frac{2\pi my}{b} \\ + \frac{2E}{a} \sum_{l=1}^{\infty} \frac{e^{-\frac{2\pi lz}{a}}}{l} \cos \frac{2\pi lx}{a} + \frac{2E}{b} \sum_{m=1}^{\infty} \frac{e^{-\frac{2\pi mz}{b}}}{m} \cos \frac{2\pi my}{b} \\ - \frac{E}{ab} 2\pi z + K_1,$$

where K_1 is a constant.

Let δ be the dipole length, and measure z from the surface downwards: $\delta E = \mu$, where μ is the electric moment. To get the potential $\phi(z)$ due to a plane array of dipoles, at the centres of spheres of radius $\frac{a}{2}$, first put $a = b$ in the expression for V , then put $z + \delta$ for z , change the sign of E , and add to the first result. This gives for points directly below the dipoles, when $x = la$, $\mu = ma$,

$$\phi(z) = 4 \frac{E}{a} \sum_{l=1}^{\infty} \sum_{m=1}^{\infty} \frac{e^{-\frac{2\pi(l^2 + m^2)z}{a}}}{(l^2 + m^2)^{\frac{1}{2}}} \left[1 - e^{-\frac{2\pi(l^2 + m^2)\delta}{a}} \right] \\ + \frac{4E}{a} \sum_{l=1}^{\infty} \frac{e^{-\frac{2\pi lz}{a}}}{l} \left[1 - e^{-\frac{2\pi l\delta}{a}} \right] + \frac{E}{a^2} \cdot 2\pi\delta + 2K_1.$$

Since $\phi(z) \rightarrow 0$ when $z \rightarrow \infty$, the last two terms together vanish. This expression may be contrasted with that for a single dipole,

$$\phi'(z) = \frac{E\delta}{z^2}.$$

If n is the concentration of either ion in the bulk of the liquid, ρ , the charge density at any point is

$$nE \left(e^{\frac{\phi E}{KT}} - e^{-\frac{\phi E}{KT}} \right) = 2nE \sinh \frac{\phi E}{KT}.$$

Here the dielectric constant of the medium has not been included, since the distances considered are comparable with molecular dimensions. The energy term due to the polarization of the adsorbed ions has also been neglected. Calculation shows that this term, $\frac{1}{2} \alpha \left(\frac{d\phi}{dz} \right)^2$, where α is the polarizability, is small.

In the expression for ρ the effect of the diffuse charge itself on the potential has been neglected, and $\phi(z)$ in the diffuse layer has been taken to be that for the dipole sheet. A second approximation to the true solution is then easily obtained as follows.

Let $f(z)$ be the true potential in the diffuse ionic layer. Then

$$\nabla^2 f'(z) = -4\pi\rho,$$

$$\frac{d^2 f}{dz^2} - 4\pi^2 \frac{(l^2 + m^2)}{a^2} f = 8\pi n E \sinh \frac{E f}{K T}.$$

The first solution above is obtained by neglecting the term on the right. To get a second approximation put

$f(z) = \phi(z)$ in $8\pi n E \sinh \frac{E f}{K T}$. The solution is then

$$\begin{aligned} f(z) = \phi(z) + \sum_{l=1}^{\infty} \sum_{m=1}^{\infty} e^{-pz} \int_{\frac{a}{2}}^z \frac{e^{pz}}{2p} 8\pi n E \sinh \frac{E \phi}{K T} . dz \\ - \sum_{l=1}^{\infty} \sum_{m=1}^{\infty} e^{pz} \int_{\frac{a}{2}}^z \frac{e^{-pz}}{2p} . 8\pi n E \sinh \frac{E \phi}{K T} . dz, \end{aligned}$$

where

$$p^2 = \frac{4\pi^2}{a^2} (l^2 + m^2).$$

The integrals are easily computed if $\sinh \frac{E \phi}{K T}$ is replaced by the empirical function $e^{\frac{-A\phi}{a}}$, since $\log \sinh \frac{E \phi}{K T}$ is roughly a straight line over the range required for the calculation below.

The correction term is then

$$\sum_{l=1}^{\infty} \sum_{m=1}^{\infty} \frac{8\pi n E a^2}{4\pi^2 (l^2 + m^2) - A^2} \left[e^{\frac{-A\phi}{a}} \right]_{\frac{a}{2}}^z,$$

and calculation shows that it is of the order of one per cent., and thus may be neglected.

The distance of the centre of gravity of the space-charge from the origin is

$$\bar{z} = \frac{\int \rho z dz}{\int \rho dz}.$$

A surface distribution $\int \rho dz$ at this point forms with the dipole sheet a three-plate condenser. If the dipole is oriented with its negative charge towards the liquid the third plate will be positive. There will be a negligible negative potential in the bulk liquid.

In the case of a spherical three-plate condenser of total charges on the plates E_1 , E_2 , E_3 , radii a , b , c ($a < b < c$), potentials V_1 , V_2 , V_3 ,

$$V_3 = \frac{E_1 + E_2 + E_3}{c},$$

$$V_2 = V_3 + (E_1 + E_2) \left(\frac{1}{b} - \frac{1}{c} \right),$$

$$V_1 = V_2 + E_1 \left(\frac{1}{a} - \frac{1}{b} \right).$$

Putting $E_1 = 4\pi a^2 \sigma_1$, $E_2 = 4\pi b^2 \sigma_2$, $E_3 = 4\pi c^2 \sigma_3$, where the σ 's are surface densities, and letting a , b , c tend to infinity, we easily get $V_1 - V_2 = 4\pi \sigma_1 d$, where d is the distance between plates 1 and 2. Thus in the case above the diffuse ionic layer contributes a work term

$$\Delta V = 4\pi \int \rho z dz = 4\pi \bar{z} \int \rho dz.$$

In the case of the fatty acid film we suppose that the COOH groups provide the electric moment considered above. The limiting area of the group COOH, from measurements on liquid condensed films, is 24.4 A.U. This gives $a = 4.94$ A.U. Debye⁽⁴⁾ gives from the effect of COOH on C_6H_6 the electric moment of the former as $9 \cdot 10^{-19}$ E.S.U. Hence $\frac{\delta}{a} = .0382$. We take the underlying liquid to be $\frac{N}{100}$ HCl.

We find that $\int \rho dz$ is $1.60 \cdot 10^3$ E.S.U. per cm.², whereas the dipole layer itself amounts to $1.96 \cdot 10^5$ E.S.U. per cm.²

Hence $\frac{V}{\Delta V}$ is about 8.7. This is of the order of $\frac{\mu}{\Delta \mu}$ obtained

by Schulman⁽⁵⁾ for myristic acid, but the sign is opposite and the film is expanded, while for palmitic acid the effect is much greater than above ($\frac{\mu}{\Delta\mu} = 1.5$), but it is of the same sign.

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XXXVI. *Graphic Statistics.*

To the Editors of the Philosophical Magazine.

GENTLEMEN,—

IN the October number of the *Philosophical Magazine* Mr. A. F. Dufton, M.A., D.I.C., gives a short note on Graphic Statistics, in which he describes a method of representing frequency distribution by means of a diagram. He proposes to call the coordinate paper with the special probability scale *Permillé* paper.

This type of paper has been used for many years by American engineers for representing water-supply statistics, and has been found very useful by this Department in representing the hydrological data collected in the Nile Basin.

The first description of this paper which I have seen is contained in an article by Allen Hazen, M.Am.Soc.C.E., published in the 'Transactions of the American Society of Civil Engineers' in December 1914, and entitled "Storage to be provided in impounding Reservoirs for Municipal Water-supply." Mr. Hazen designed the coordinate paper with the probability scale to represent the statistics involved in this article, and he called it "Probability Paper." This name has been used fairly widely since.

Yours faithfully,

P. PHILLIPS.

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XXXVII. *Permillé Paper.**To the Editors of the Philosophical Magazine.*

GENTLEMEN,—

SINCE the publication in the October number of the *Philosophical Magazine* of my note on Graphic Statistics, I have received inquiries as to whether *Permillé* paper would be printed and generally available, one firm writing that the paper would be of very great assistance to them.

My attention has kindly been drawn by Mr. J. H. Awbery to the description, in Tuttle and Satterly's 'Theory of Measurements,' of similar section paper designed by Messrs. Hazen, Whipple and Fuller and published under the name of Arithmetic Probability Paper by the Codex Book Co. of New York.

I hope that this information will assist those who, like myself, were ignorant of this paper.

A. F. DUFTON.

7th November, 1930.

XXXVIII. *Proceedings of Learned Societies.*

GEOLOGICAL SOCIETY.

[Continued from vol. x. p. 968.]

November 5th, 1930.—Prof. E. J. Garwood, M.A., Sc.D., F.R.S.,
President, in the Chair.

THE following communications were read:—

1. 'The Geology of the Dolwyddelan Syncline (North Wales).' By Howel Williams, M.A., D.Sc., D.I.C., F.G.S., and Oliver Meredith Boone Bulman, Ph.D., D.I.C., A.R.C.Sc., F.G.S.

The syncline lies east of Snowdon and south of Capel Curig, extending along the Lledr Valley westwards from the village of Dolwyddelan. The rock-sequence is closely comparable with that determined by the senior author on Snowdon, and the pyroclastic rocks of Dolwyddelan are, in effect, the attenuated and ragged margin of the great Snowdonian volcanic mass. The following succession is represented:—

		Thickness in feet.
MIDDLE CARADOCIAN.	Black Slates.	100
	Snowdon Volcanic Suite.	
	{ Upper Rhyolite-Tuffs, with pyritous black mud-nodules near the top	100 to 650
! MIDDLE CARADOCIAN.	{ Bedded Pyroclastic Series: andesitic and basaltic pumice-tuffs	up to 800
	{ Lower Rhyolite-Tuffs: potash- rhyolite-tuffs becoming in- creasingly muddy eastwards.	200 to 700
	{ Flinty Rhyolites of Cerrig Cochion	800
? LOWER CARADOCIAN & UPPER LLANDEILIAN.	{ Glanrafon Beds, with inter- bedded rhyolites and tuffs: generally more slaty east- wards	2500

The flinty rhyolites of Snowdon, although absent in the Dolwyddelan Syncline proper, occur at the margin of the area mapped (on Cerrig Cochion) where they overlie, and all but obscure, a small flow of the basal Pitt's Head lava.

The pyroclastic rocks in general thin out rapidly eastwards and southwards, and local variations in thickness are probably due to deposition on an extremely irregular sea-floor.

The graptolite fauna of the Black Slates furnishes an upper time-limit for the Snowdonian vulcanicity, and this may be assigned to the upper part of the Zone of *Dicranograptus clingani*. Rather less certain is the evidence for the age of the upper Glanrafon Beds which underlie the volcanic series, but it cannot be placed much below the Middle Caradocian. Possibly, therefore, the Snowdon lavas and tuffs correspond to no more than the lower part of the *Dicranograptus-clingani* Zone, but the necessity of collating shelly and graptolitic faunas introduces some uncertainty.

The central portion of the northern limb of the syncline has been overturned, much as has the northern limb of the Snowdon Syncline, and in both cases the cleavage-dip diminishes in the zone of inversion from the normal regional angle of 70°-80° to one of 30°-40°. West of the area of maximum inversion, there is evidence, in the subsidiary lava-syncline of Afon Diwaunedd, of small-scale isoclinal folding, such as might precede the development of imbricate structure, but in the syncline itself there is no indication of such folding, neither is there any indication of large-scale thrusting. The field-evidence, however, suggests the occurrence of a multiplicity of glide-planes, mostly coinciding with the planes of cleavage. The Authors incline to the view that the overturning of the northern limb was accomplished by a kind of 'under-drive', much of which took place prior to and during the impression of cleavage, but the final stages of which seem to have been part of a general post-cleavage movement.

Large bodies of fresh augite-dolerite, well developed along the northern limb of the syncline, testify to the post-cleavage intrusion of basic magmas.

2. 'Jointing in the Great Scar Limestone of Craven, and its Relation to the Tectonics of the Area.' By Lawrence Rickard Wager, F.G.S.

The Great Scar Limestone of Craven is traversed by two sets of nearly vertical joints, which are usually at right angles one to the other. Some 4 miles north-west of Grassington-in-Wharfedale, the lead-veins run parallel to one set of the joints, and were in fact deposited in widened joints. The joints and mineral veins are constant in direction over a considerable area; but, as the North Craven Fault is approached, their direction is modified. These preliminary observations showed that the formation of the joints preceded the mineralization, which is probably of pre-Permian age, and suggested that the jointing and the Craven Faults may be related in some way, since the modification in the direction of the joints is localized near the faults.

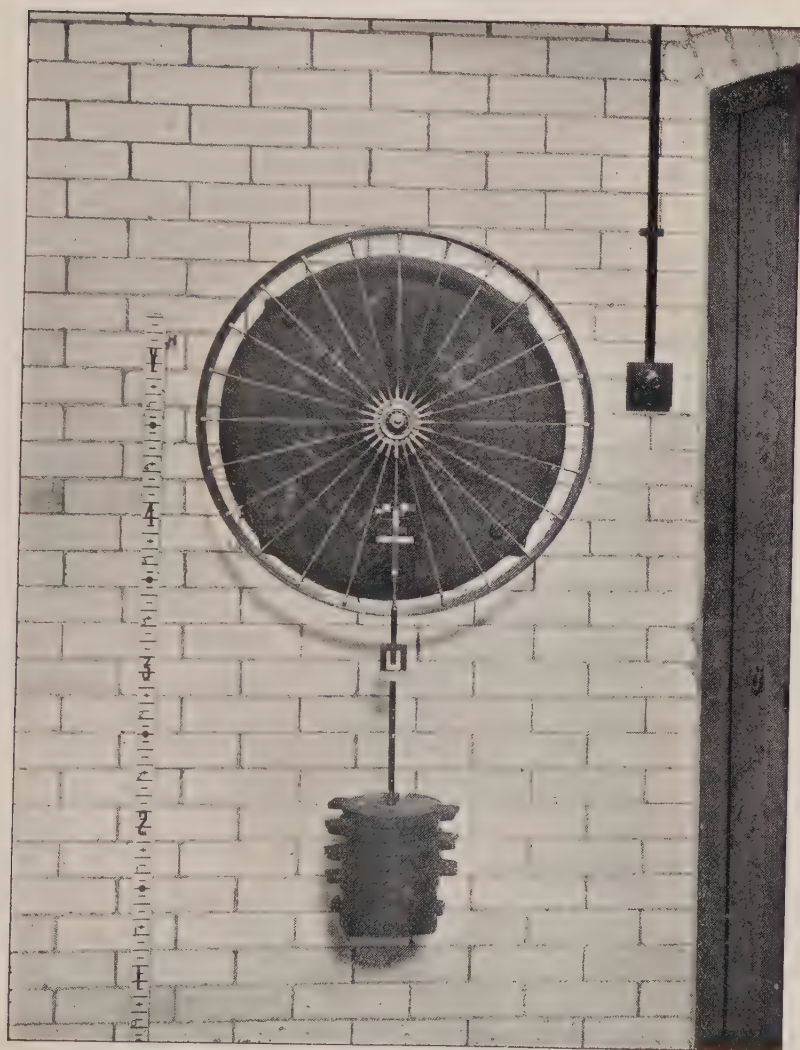
In order to test this hypothesis, the joints have been examined over a wide area, and a map has been made showing the direction of the jointing in the Great Scar Limestone between Dentdale and Wensleydale and the Dent and Craven Faults. The character of individual joint-planes and of the joint-pattern is considered to indicate that the normal joints were formed, as shearing fractures, at approximately 45° to a maximum horizontal compressive stress in the Earth's crust.

The rotation of the joints near the Craven Faults can be explained, if the North Craven Fault and, to some extent, the Middle Craven Fault are considered as tear-faults. The country north of the North Craven Fault is believed to have moved north-westwards relative to the country on the south.

Evidence is given that the time of formation of the joints was early in the interval between the Westphalian and the Saxonian. The Hercynian compression which produced the contemporary Dent Fault, the Middleton Tyas anticline, and the folding in Southern Craven is considered to have been also responsible for the formation of the joints and the tear-faults. The different ways in which the Craven and surrounding areas yielded to the Hercynian compression are traced to differences in the depth of burial of the pre-Carboniferous floor.

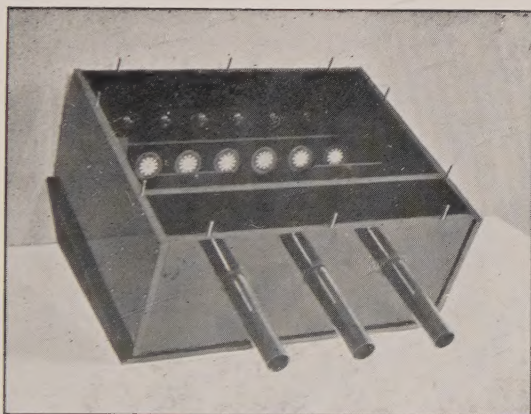
The main throw of the Craven Faults and much of the minor faulting which follows the direction of the joints are considered to be later, and not directly connected with the effects of the Hercynian compression.

[The Editors do not hold themselves responsible for the views expressed by their correspondents.]



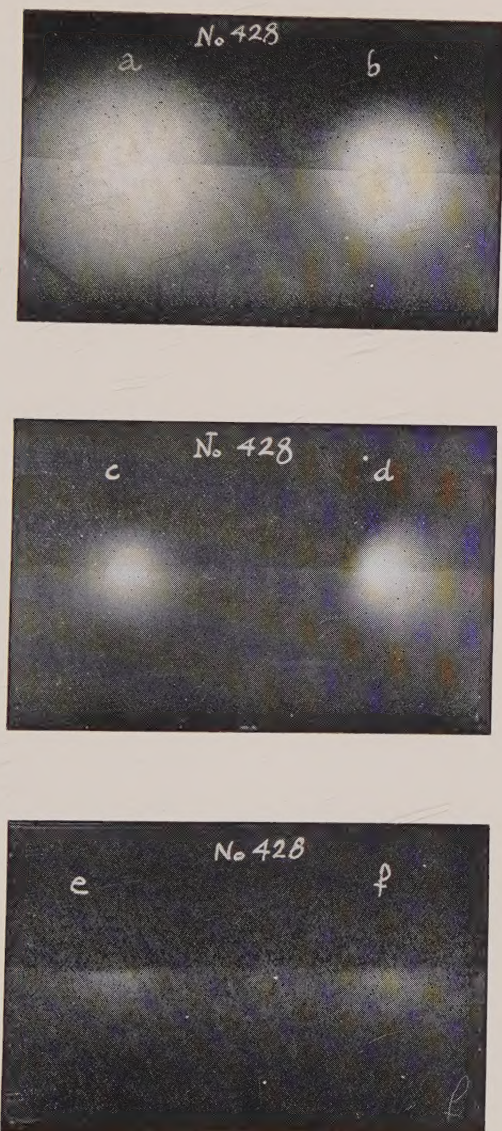
Arrangement of experimental wheel.

FIG. 2.



The light-tight box, with six radiating cells and film holders.

FIG. 4.



The effect produced by the radiating cells on the photographic films
The upper part of the films was covered with a sheet of celluloid
·13 mm. thick.

